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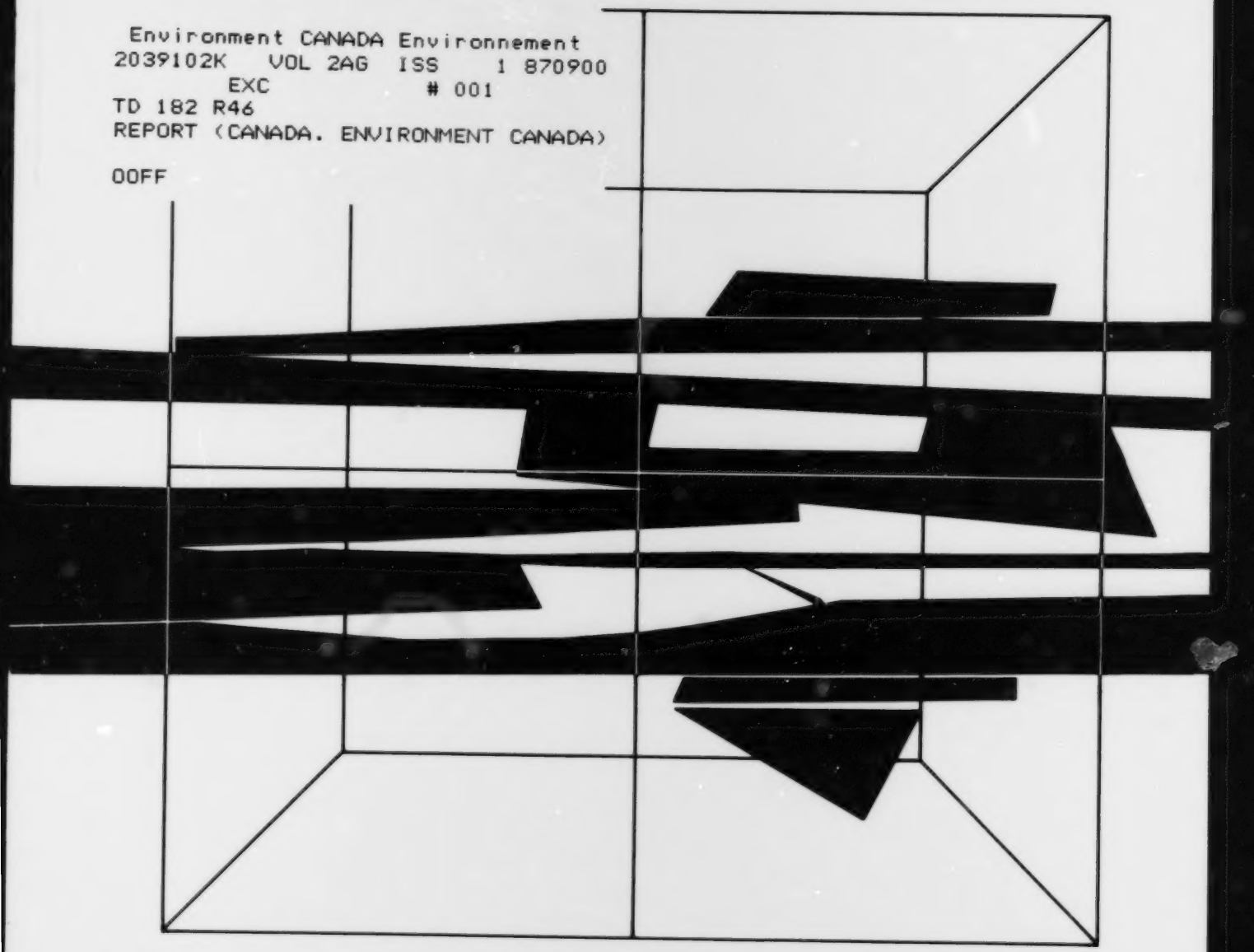

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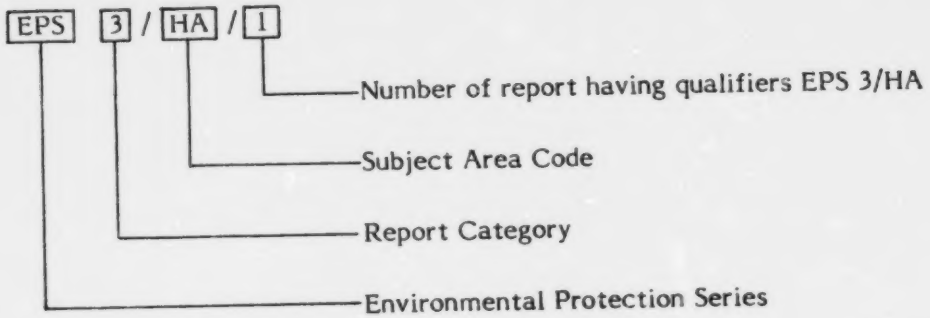

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REVIEW OF THE CANADIAN FERTILIZER INDUSTRY AND EVALUATION OF CONTROL TECHNOLOGY

by

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Report EPS 2/AG/1
September 1987

READERS' COMMENTS

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ABSTRACT

This report reviews basic background information on the processes used in the fertilizer industry, waste products produced and their disposal practices, air emission loadings to atmosphere from unit processes and current control practices, recycle/reuse and other waste reduction practices, water uses, wastewater treatment practices, and concentrations and loadings of conventional and toxic contaminants discharged in the final effluent from these plants. The information is based on questionnaire surveys, visits to fertilizer plants, company-supplied data, and literature surveys.

Solid wastes produced at nitrogen fertilizer plants consist mainly of domestic garbage, minor amounts of contaminated solid fertilizer, and used catalysts that are stored for safe disposal or sold for metal recovery. Gypsum, acid sludge, and scrubber solids from the production of phosphate fertilizers normally go to contained gypsum ponds. The major environmental concerns regarding gypsum ponds are groundwater contamination and the source of low-level radioactivity.

The major emission problems associated with the manufacture of nitrogen fertilizers are oxides of nitrogen from the primary reformer and nitric acid plants, ammonia from the regeneration of carbon dioxide scrubbing solution, and ammonia and particulates from unit processes in the manufacture of urea and ammonium nitrate. The major emission problems associated with the manufacture of phosphate fertilizers are primarily particulates and gaseous fluorides.

Wastewater contaminant loadings in effluents discharged from phosphate fertilizer plants are minor as all process effluents and scrubber wastewaters are recycled to the gypsum pond. The main contaminants present in the process wastewater from nitrogen fertilizer plants are ammonia nitrogen, nitrate nitrogen, and organic nitrogen. Most of the plants have developed ways of recovering these nitrogen values. The process changes and wastewater treatment changes made at all fertilizer plants have significantly reduced conventional pollutant concentrations in the wastewaters discharged. Biological testing of these effluents elicited no genotoxic activity using (unconcentrated) straight effluents.

The federal and some provincial environmental agencies are evaluating the requirements to prevent the dispersal of radionuclides by air and water from phosphogypsum ponds. Apart from the phosphogypsum, the report concludes that further regulatory initiatives by the federal government are not required at this time.

RÉSUMÉ

Ce rapport examine l'information de base dans les domaines suivants: procédés utilisés dans l'industrie des engrais; déchets produits et méthodes d'élimination; émissions atmosphériques inhérentes aux procédés industriels et techniques antipollution actuellement mises en oeuvre; recyclage, réutilisation et autres pratiques pour réduire la quantité de déchets; utilisation de l'eau; techniques d'épuration des eaux usées; teneurs et charges en polluant habituels et en produits toxiques dans l'effluent terminal des usines d'engrais. L'information est fondée sur des enquêtes avec questionnaires, des visites d'usines d'engrais, des renseignements fournis par les compagnies, et des données recueillies dans la documentation scientifique.

Les déchets solides produits par les usines d'engrais azotés sont principalement constitués de déchets domestiques, de petites quantités d'engrais solides pollués, et de catalyseurs usés qui sont entreposés en vue de leur élimination sans risque pour l'environnement, ou de leur vente pour la récupération du métal. Les déchets résultant de la production d'engrais phosphatés, soit le gypse, les solides contenus dans les liquides de lavage, et les boues acides, sont généralement déversés dans des bassins à gypse. La principale menace pour l'environnement que posent ces bassins est la pollution des eaux souterraines et le danger d'apparition d'un faible niveau de radioactivité.

Les polluants les plus préoccupants liés à la production d'engrais azotés, et leurs sources, sont: les oxydes d'azote provenant du reformage primaire et des usines d'acide nitrique; l'ammoniac provenant de la régénération des solutions d'épuration du CO_2 et de l'épuration des condensats; l'ammoniac et les particules provenant de la fabrication de l'urée et du nitrate d'ammonium. En ce qui concerne la fabrication des engrais phosphatés, les fluorures gazeux et les particules solides retiennent particulièrement l'attention.

La charge en polluants de l'effluent terminal des usines d'engrais phosphatés est faible, car toutes les eaux résiduaires ainsi que les liquides de lavage sont recyclés dans le bassin à gypse. Les principaux polluants présents dans les eaux résiduaires de fabrication des engrais azotés sont l'ammoniac, l'azote nitrique et l'azote organique. La plupart des usines ont mis au point des procédés pour récupérer les produits azotés. Les modifications apportées aux procédés de fabrication et aux méthodes d'épuration dans toutes les usines d'engrais ont sensiblement réduit les teneurs en polluants habituels dans l'effluent terminal. Des bio-essais effectués avec ces effluents (bruts, non concentrés) n'ont révélé aucune activité génotoxique.

Le gouvernement fédéral et certains organismes environnementaux provinciaux examinent actuellement des moyens pour empêcher la dispersion de radionucléides par évaporation et infiltration d'eau des bassins à gypse. Il ressort de cette étude que la seule autre mesure de réglementation à envisager pour le moment soit celle touchant les radionucléides en provenance des bassins à gypse.

TABLE OF CONTENTS

		Page
ABSTRACT		iii
RÉSUMÉ		iv
LIST OF FIGURES		ix
LIST OF TABLES		xi
ACKNOWLEDGEMENTS		xiii
EXECUTIVE SUMMARY		xv
1	INTRODUCTION	1
1.1	Background	1
1.2	Objectives of the Study	1
1.3	General Approach and Methodology	2
2	DESCRIPTION OF THE CANADIAN FERTILIZER INDUSTRY	3
2.1	Nitrogen Fertilizers	3
2.1.1	Anhydrous Ammonia	5
2.1.2	Ammonium Nitrate	5
2.1.3	Urea	7
2.1.4	Ammonium Sulphate	7
2.1.5	Nitric Acid	8
2.1.6	Nitrogen Solutions	8
2.2	Phosphate Fertilizers	8
2.2.1	Ammonium Phosphate	10
2.2.2	Phosphoric Acid	11
3	PROCESS DESCRIPTION	12
3.1	Nitrogen Fertilizer Production Processes	12
3.1.1	Anhydrous Ammonia	12
3.1.2	Ammonium Nitrate	17
3.1.3	Urea	20
3.1.4	Ammonium Sulphate	23
3.1.5	Nitric Acid	23
3.2	Phosphate Fertilizer Production Processes	27
3.2.1	Phosphate-Rock Grinding	27
3.2.2	Phosphoric Acid	28
3.2.3	Normal Superphosphate	30
3.2.4	Triple Superphosphate	32
3.2.5	Ammonium Phosphate	32
3.2.6	Sulphuric Acid	34

		Page
4	WASTEWATER SOURCES AND CHARACTERISTICS	39
4.1	Nitrogen Fertilizer Industry	39
4.1.1	Water Use	39
4.1.2	Wastewater Sources	40
4.1.3	Wastewater Characteristics	42
4.2	Phosphate Fertilizer Industry	48
4.2.1	Water Use	48
4.2.2	Wastewater Sources	49
4.2.3	Wastewater Characteristics	52
4.3	Sampling and Analytical Procedures	56
4.3.1	Monitoring and Recording Procedures Used by Companies	56
4.3.2	Analytical Methods Used by Companies	56
4.3.3	Methods Used in the Screening Survey	56
5	EMISSION SOURCES AND CHARACTERISTICS	63
5.1	Emission Sources from Nitrogen Fertilizer Plants	63
5.1.1	Ammonia Plants	63
5.1.2	Ammonium Nitrate Plants	63
5.1.3	Urea Plants	63
5.1.4	Ammonium Sulphate Plants	63
5.1.5	Nitric Acid Plants	63
5.2	Air Emission Characteristics	64
5.2.1	Ammonia Plants	64
5.2.2	Ammonium Nitrate Plants	66
5.2.3	Urea Plants	68
5.2.4	Ammonium Sulphate Plants	69
5.2.5	Nitric Acid Plants	69
5.3	Emission Sources from Phosphate Fertilizer Plants	70
5.3.1	Sulphuric Acid Plants	70
5.3.2	Phosphate-Rock Grinding	70
5.3.3	Phosphoric Acid Plants	70
5.3.4	Normal Superphosphate Plants	71
5.3.5	Triple Superphosphate Plants	71
5.3.6	Ammonium Phosphate Plants	71
5.4	Air Emission Characteristics	72
5.4.1	Sulphuric Acid Plants	72
5.4.2	Phosphate-Rock Grinding	72
5.4.3	Phosphoric Acid Plants	72
5.4.4	Normal Superphosphate Plants	72
5.4.5	Triple Superphosphate Plants	73
5.4.6	Ammonium Phosphate Plants	73
6	SOLID WASTE SOURCES AND CHARACTERISTICS	75
6.1	Solid Wastes from Nitrogen Fertilizer Plants	75
6.1.1	Ammonia Plants	75
6.1.2	Ammonium Nitrate Plants	75
6.1.3	Urea Plants	75

		Page
6.1.4	Ammonium Sulphate Plants	75
6.1.5	Nitric Acid Plants	75
6.2	Solid Wastes from Phosphate Fertilizer Plants	76
6.2.1	Sulphuric Acid Plants	76
6.2.2	Phosphate-Rock Grinding	76
6.2.3	Phosphoric Acid Plants	76
6.2.4	Ammonium Phosphate Plants	76
6.2.5	Normal and Triple Superphosphate Plants	76
7	WASTEWATER CONTROL AND TREATMENT TECHNOLOGY	77
7.1	Nitrogen Fertilizer Industry	77
7.1.1	Available Technology	77
7.1.2	Water Pollution Control Measures	91
7.2	Phosphate Fertilizer Industry	97
7.2.1	Available Technology	97
7.2.2	Water Pollution Control Measures	103
7.3	Screening and Verification Program	109
7.3.1	Purpose and Method	109
7.3.2	Methodology	110
7.3.3	Results	110
7.3.4	Discussion	113
8	AIR EMISSIONS CONTROL AND TREATMENT TECHNOLOGY	122
8.1	Nitrogen Fertilizer Industry	122
8.1.1	Available Technology	122
8.1.2	Air Emission Control Measures	137
8.2	Phosphate Fertilizer Industry	150
8.2.1	Available Technology	150
8.2.2	Air Emission Control Measures	156
8.2.3	Gypsum Pond Emissions	167
9	ENVIRONMENTAL IMPACT	169
9.1	Wastewater Discharged from Fertilizer Plants	169
9.1.1	Nitrogen Fertilizer Plants	169
9.1.2	Phosphate Fertilizer Plants	170
9.2	Discharge Quantities	171
9.3	Receiving Body of Water	172
9.4	Environmental Impact on the Receiving Body	172
REFERENCES		175
GLOSSARY		179
APPENDIX A	PROVINCIAL EFFLUENT GUIDELINES AND STANDARDS FOR THE FERTILIZER INDUSTRY	187

		Page
APPENDIX B	MONITORING AND EFFLUENT CONTROL MEASURES USED AT NITROGEN AND PHOSPHATE FERTILIZER PLANTS	193
APPENDIX C	SCREENING SURVEY AT FERTILIZER PLANTS	205
APPENDIX D	EFFLUENT CHARACTERISTICS OF UNTREATED COOLING WATER, COMPRESSOR AND BOILER BLOWDOWN, AND SCRUBBER SOLUTIONS	217
APPENDIX E	RESULTS OF BIOLOGICAL TESTING OF FERTILIZER PLANT FINAL EFFLUENT FOR GENOTOXIC ACTIVITY	223

LIST OF FIGURES

Figure		Page
1	NITROGEN FERTILIZER PLANT LOCATIONS IN CANADA	4
2	PHOSPHATE FERTILIZER PLANT LOCATIONS IN CANADA	9
3	PROCESS FLOW SHEET - AMMONIA PRODUCTION	13
4	PROCESS FLOW SHEET - AMMONIUM NITRATE PRODUCTION	18
5	PROCESS FLOW SHEET - UREA PRODUCTION	21
6	PROCESS FLOW SHEET - AMMONIUM SULPHATE PRODUCTION	24
7	PROCESS FLOW SHEET - NITRIC ACID PRODUCTION	25
8	PROCESS FLOW SHEET - WET PROCESS PHOSPHORIC ACID PRODUCTION	29
9	PROCESS FLOW SHEET - NORMAL SUPERPHOSPHATE PRODUCTION	31
10	PROCESS FLOW SHEET - TRIPLE SUPERPHOSPHATE PRODUCTION	33
11	PROCESS FLOW SHEET - AMMONIUM PHOSPHATE PRODUCTION	35
12	PROCESS FLOW SHEET - SULPHURIC ACID PRODUCTION	36
13	SUMMARY OF NITROGEN FERTILIZER COMPLEX EFFLUENT TREATMENT PROCESSES	80
14	AMMONIA PROCESS CONDENSATE AIR STRIPPING UNIT	82
15	AMMONIA PROCESS CONDENSATE TREATMENT STEAM STRIPPER UNIT	84
16	AMMONIA PROCESS CONDENSATE TREATMENT INERT GAS - STEAM STRIPPER UNIT	85
17	NITROGEN FERTILIZER COMPLEX PROCESS EFFLUENT TREATMENT - CONVENTIONAL COUNTERCURRENT ION EXCHANGE UNIT	87
18	COOLING WATER BLOWDOWN TREATMENT - CHROMATE AND ZINC REDUCTION	90
19	SUMMARY OF PHOSPHATE FERTILIZER COMPLEX EFFLUENT TREATMENT PROCESSES	98

Figure		Page
20	FLUORIDE AND PHOSPHATE REMOVAL - MULTISTAGE LIMING TREATMENT	101
21	SCRUBBING AND LIME TREATMENT PROCESS FOR PHOSPHATE FERTILIZER PLANTS WITHOUT GYPSUM POND	101
22	PRILL TOWER DUST COLLECTION DUCT	127
23	TRAY-TYPE SCRUBBER	129
24	SPRAY TOWER SCRUBBER	129
25	IMPINGEMENT SCRUBBER	131
26	WET CYCLONE SCRUBBER	132
27	"CHEAF" SCRUBBER, ANDERSEN 2000 INC.	136
28	SPRAY - CROSS-FLOW PACKED BED SCRUBBER	151
29	CYCLONIC SPRAY TOWER SCRUBBER	152
30	TELLER COAXIAL SCRUBBER	154

LIST OF TABLES

Table		Page
1	PRODUCTION CAPACITY OF NITROGEN FERTILIZER PLANTS IN CANADA	6
2	CHEMICAL ANALYSIS OF PHOSPHATE ROCK, AS REPORTED BY CANADIAN FERTILIZER MANUFACTURERS	10
3	PRODUCTION CAPACITY OF PHOSPHATE FERTILIZER PLANTS IN CANADA	11
4	NITROGEN FERTILIZER PLANTS FINAL EFFLUENT CHARACTERISTICS	44
5	COMPOSITION OF A TYPICAL COOLING TOWER BLOWDOWN FROM A NITROGEN FERTILIZER COMPLEX	45
6	COMPOSITION OF A TYPICAL BOILER BLOWDOWN	46
7	VOLUME AND COMPOSITION OF PROCESS EFFLUENTS FROM VARIOUS NITROGEN FERTILIZER PLANTS	47
8	CHARACTERISTICS OF WASTEWATER FROM PHOSPHATE FERTILIZER PLANTS	53
9	TYPICAL ANALYSIS OF GYPSUM POND WATER	54
10	COMPOSITION OF A TYPICAL COOLING TOWER BLOWDOWN FROM A PHOSPHATE FERTILIZER COMPLEX	55
11	SUMMARY OF PRIORITY METAL CONCENTRATIONS FOUND IN THE FINAL EFFLUENT FROM NITROGEN FERTILIZER PLANTS	57
12	SUMMARY OF PRIORITY METAL CONCENTRATIONS FOUND IN THE FINAL EFFLUENT FROM PHOSPHATE FERTILIZER PLANTS	58
13	PRIORITY ORGANIC POLLUTANTS FOUND IN THE FINAL EFFLUENT FROM FERTILIZER PLANTS: CONCENTRATION RANGE AND AMBIENT WATER QUALITY CRITERIA PROPOSED BY EPA	61
14	WATER POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS	92
15	WATER POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS	104
16	SUMMARY OF TESTING OF EFFLUENT SAMPLES	113
17	SUMMARY OF *Salmonella* MUTAGENICITY TEST RESULTS	114

Table		Page
18	PRIORITY POLLUTANTS FOUND IN FINAL EFFLUENT FROM FERTILIZER PLANTS AND THEIR AQUATIC FATE AND POSSIBLE TREATMENT METHODS	118
19	AIR POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS	138
20	AIR EMISSIONS FROM NITROGEN FERTILIZER PLANTS	146
21	AIR POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS	158
22	AIR EMISSIONS FROM PHOSPHATE FERTILIZER PLANTS	166
23	CALCULATED ENVIRONMENTAL IMPACT FOR PLANTS PRODUCING NITROGEN FERTILIZERS	173

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EXECUTIVE SUMMARY

At present, there are 12 nitrogen fertilizer plants in Canada producing around 4.1 million tonnes of anhydrous ammonia, 1.0 million tonnes of ammonium nitrate, 2.5 million tonnes of urea, 0.35 million tonnes of ammonium sulphate, and 1.0 million tonnes of nitric acid. In addition, there are six phosphate fertilizer plants producing around 0.80 million tonnes of phosphoric acid (as P_2O_5), 1.9 million tonnes of ammonium phosphate, and 1.9 million tonnes of sulphuric acid for fertilizer use at the six plants. Most plants are operating under provincial control orders, which set emission levels to meet ministerial objectives and establish contaminant limits for any wastewaters discharged from the plants.

This report reviews production processes; waste products produced and disposal practices; air emission loadings to the atmosphere from unit processes and current control practices, recycle/reuse, and other waste reduction practices; wastewater treatment practices; and concentrations and loadings of conventional and toxic contaminants discharged in the final effluent from these fertilizer plants.

Synthetic ammonia is mainly produced in Canada by catalytic reforming of natural gas using a seven-step process. Nitric acid solution is produced in a three-step ammonia oxidation process by which ammonia is catalytically oxidized to NO and further oxidized to NO_2. The NO_2 then reacts with water to form HNO_3 and NO. Ammonium nitrate solution is produced by an exothermic reaction between ammonia and nitric acid. The ammonium nitrate produced is sold as a solution, mixed with other fertilizers, or converted to a solid form by various processes. Urea is produced in a two-step reaction in which ammonia and carbon dioxide react to form ammonium carbamate, which is then dehydrated to form urea and water. Ammonium sulphate solution is produced by an exothermic reaction between ammonia and sulphuric acid. The product is normally crystallized, dried, and mixed with other fertilizers. Phosphoric acid is the most important intermediate manufactured by the phosphate fertilizer industry because it is a basic ingredient in every phosphate fertilizer product except normal superphosphate. Wet phosphoric acid is produced by the digestion of phosphate rock with sulphuric acid. Sulphuric acid is produced by a contact process incorporating three basic operations: burning of sulphur or sulphur-bearing feedstocks to form SO_2, catalytic oxidation of SO_2 to SO_3, and absorption of SO_3 in a strong acid stream. Normal superphosphate involves reacting phosphate rock with sulphuric acid to form monocalcium phosphate. Triple superphosphate involves reacting phosphate rock with phosphoric acid to produce a

fertilizer containing 46 to 48% P_2O_5. Ammonium phosphate is manufactured by the neutralization of phosphoric acid with ammonia under controlled conditions to produce either mono- or di-ammonium phosphate. The product is converted to a solid form by various processes.

Solid wastes produced at nitrogen fertilizer plants consist mainly of domestic garbage and minor amounts of contaminated solid fertilizer, which are disposed of at sanitary landfill sites, and used catalysts, which are stored for eventual safe disposal or sold for metal recovery. Gypsum, acid sludge, and scrubber solids from the production of phosphate fertilizers normally go to contained gypsum ponds. Several potential solid waste recovery methods are feasible; however, none are economical. The major environmental concerns regarding gypsum ponds are groundwater contamination and the source of low-level radioactivity.

The major emission problems associated with the manufacture of nitrogen fertilizers are ammonia, oxides of nitrogen resulting from the addition of purge gas and overhead (at one plant) to the radiant heat section of the primary reformer, and particulates from the prilling of ammonium nitrate and urea. Newer plants have no stripper overheads, purge gas is recovered by cryogenic means, and other methods, besides prill towers, are used for the solidification of urea and ammonium nitrate.

The major emission problems associated with the manufacture of phosphate fertilizers are particulates and gaseous fluorides. Emission control devices have been installed in all plants, which have reduced particulate and fluoride emissions to the best practicable control technology level.

Wastewater contaminant loadings in effluents discharged from phosphate fertilizer plants are minor as all process effluents and scrubber wastewaters are recycled to the gypsum pond. Any wastewaters discharged are cooling water; cooling tower, compressor, and boiler blowdown; and raw water treatment wastes.

Effluents from a nitrogen fertilizer plant originate from a variety of point and nonpoint sources. The major components in the effluent are ammonia nitrogen, nitrate nitrogen, and organic nitrogen. Low concentrations of other constituents are also present. The potential environmental impact of nitrogen fertilizer effluents was evaluated by comparing the concentration of a particular pollutant in a receiving stream as a result of a discharge with an acceptable water quality criterion concentration.

The process changes, nitrogen containing wastewater recovery practices, and treatment changes made at all fertilizer plants have significantly reduced conventional pollutant concentrations in the wastewaters discharged. Nevertheless, about 25 or

30 chlorinated organic contaminants were found, as well as a number of metals. The metallic concentrations in the final effluent are too low to be treatable by conventional techniques. The organic pollutant concentrations are also low, ranging in concentrations from trace levels to 2360 µg/L.

In vitro mutagenicity testing of these effluents elicited no genotoxic activity using straight effluents. These same samples when concentrated 250-fold by extraction elicited mutagenic response under some test conditions. Positive results from *in vitro* mutagenicity tests cannot be interpreted directly as an indication of hazard, although such data require confirmation by whole-animal studies.

Federal and two provincial environmental agencies are evaluating the requirements to prevent the dispersal of radionuclides by air and water from phosphogypsum ponds. Apart from the phosphogypsum, the report concludes that further regulatory initiatives by the federal government are not required at this time.

Further conclusions and recommendations include the following:

1) Fertilizer plant locations and sizes are as follows:

Product	Location	Plant Size (t/d)
Anhydrous Ammonia	80% Alberta, British Columbia, Manitoba	180-2400
	20% Ontario	225-1100
Ammonium Nitrate	50% Alberta, Manitoba	100-600
	50% Ontario	400-500
Urea	87% Alberta	200-1650
	13% Ontario	300-550
Nitric Acid	37% Alberta, Manitoba	100-600
	63% Ontario	350-850
Phosphoric Acid	78% Alberta, British Columbia	140-760
	22% Ontario, New Brunswick	170-400
Ammonium Phosphate	80% Alberta, British Columbia	340-2000
	20% Ontario, New Brunswick	330-800
Sulphuric Acid*	100% Alberta, British Columbia	600-1600

* produced at the fertilizer complex

2) In Canada, approximately 98.0% of synthetic ammonia is produced by catalytic reforming of natural gas using a seven-step process. The other 2.0% is produced by the partial oxidation of natural gas process.

3) Natural gas feedstock for the production of ammonia is desulphurized using activated carbon beds or zinc oxide beds. Steam regeneration of the former can result in air emissions of hydrocarbons, CO, and SO_2. Regeneration is intermittent and emissions are low; thus, controls should not be required. Newer ammonia plants

in Canada utilize zinc oxide beds, which result in energy savings because these beds are not regenerated.

4) The heat for the reaction in the primary reformer is supplied by firing natural gas, yielding typical combustion products. Most of the older ammonia plants are adding purge gas from the ammonia synthesis loop to the primary reformer, which reduces emissions from this source but increases NO_x emissions from the reformer stack. Instead of firing the reformer with purge gas, two of the newest plants are using a cryogenic recovery system.

5) Regeneration of carbon dioxide scrubbing solutions generates a gas containing approximately 98.5% CO_2, with small amounts of water vapour, ammonia, hydrocarbons, and CO. Eight plants use part of this gas to produce urea and five plants use some of the gas to produce liquid carbon dioxide and/or dry ice; the rest of the gas goes to the atmosphere.

6) Wastewater from ammonia, ammonium nitrate, and urea plants in Canada, which is mainly process condensate, spills, and leaks from valves and pumps, is used in the following ways: to make liquid nitrogen fertilizers; to irrigate adjacent land; the ammonia content in the condensate is removed by ion exchange and the regenerated $(NH_4)_2SO_4$ is sent to the phosphate fertilizer plant; is steam stripped and the effluent is reused in the boiler house or other parts of the plant; and the effluent is reused as is in other parts of the plant. These systems have reduced the nitrogen content in the wastewaters discharged to fairly low levels in all plants where they have been introduced.

7) Techniques used to abate ammonium nitrate plant emissions and levels attained are as follows:

		Emissions	
Source	Controls	NH_3 (kg/t)	Particulates (kg/t)
Neutralizer	Demister, Brinks scrubber, condenser, scrubbers	0-0.85 (0.48)	0-2.5 (0.27)
Evaporator/ concentrator	Wet scrubbers, scrubber plus condenser, no control	0-0.23 (0.10)	Low, no values
Prill tower	Collection cone and Brinks scrubber (1), Brinks scrubber (3), no control for rest	0.10	0.11-7 (0.80)
Dryers and loading	Baghouse (5), no control for rest	-	0.025

Note: averages in parentheses

8) Techniques used to abate NO_x emissions in the tail gas exiting the absorbers in nitric acid plants and levels attained are as follows:

Source	Controls	NO_x Emissions (kg/t)
Tail gas	Catalytic converter, molecular sieve, dual catalytic converter, extended absorption, Goodpasture system	0.33-5.96 (2.14)

Note: average in parentheses

9) Techniques used to abate urea plant emissions and levels attained are as follows:

		Emissions	
Source	Controls	NH_3 (kg/t)	Particulates (kg/t)
Reactor	Decomposer and scrubber and wash column, off gas to ammonium nitrate plant	No emissions	
Evaporator/ concentrator	Condensers, scrubber and demister, to ammonium nitrate plant, no control	(1.2)	(0.58)
Granulator	Wet scrubbers (5)	(1.45)	(0.32)
Prill towers	CHEAF scrubber (1), no control (2)	(1.2)	(0.50)

Note: averages in parentheses

The tower with the CHEAF scrubber has very low ammonia and particulate emissions.

10) Zinc oxide beds that have been used for the desulphurization of natural gas will be sold for metal recovery or disposed of at a controlled landfill site. Utilized catalyst is sold to scrap dealers for metal recovery or disposed of at landfill sites. Otherwise, there are little solid wastes from nitrogen fertilizer plants.

11) Techniques used to abate emissions from phosphate-rock handling facilities and levels attained are as follows:

Source	Controls	Particulate Emissions
Rock handling	Baghouses, wet impinger scrubber	Not enough measurements

12) Techniques used to abate emissions from phosphoric acid plants and levels attained are as follows:

Source	Controls	Emissions (F, kg/t P_2O_5 equivalent)
Digester, filter, seal tanks, feed tanks, etc.	Cross-flow packed scrubber (6)	0.004–0.113 (0.028)
	Impinger scrubbers in series (1)	0.17

Note: average in parentheses

13) Techniques used to abate emissions from ammonium phosphate plants and levels attained are as follows:

		Emissions (kg/t)			
Source	Controls	NH_3	F	P_2O_5	Particulate
Reactor	Wet scrubbers				
Granulator	Wet scrubbers (normally the same scrubber as used for reactor)	Emissions from all units: 2.0	0.053	0.04	0.46
Screens, dryer, etc.	Cyclones and wet scrubbers				

14) Techniques used to abate emissions from sulphuric acid plants and levels attained are as follows:

Source	Controls	Emissions (kg/t)		
		SO_2	SO_3	Acid Mist
Acid stack	Double absorption plus Brinks mist eliminators, metallurgical gas cleaned with gas cleaner and electrostatic precipitator (ESP)	(8.5)	(0.04)	(0.04)

Note: averages in parentheses

15) Air contaminant emissions from all fertilizer and precursor plants in Canada are estimated to be as follows:

Source	Nitrogen Oxides (as NO_2)	Ammonia	Fluoride	Sulphur Dioxide	Particulates
Ammonia	7 490	2 020	-	8.0	-
Nitric Acid	2 035	-	-	-	-
Ammonium Nitrate	-	640	-	-	764
Urea	-	6 160	-	-	1 717
Phosphoric Acid	-	-	31	-	1 250*
Ammonium Phosphate	-	3 960	107	-	920
Sulphuric Acid	-	-	-	11 500	-
TOTAL	9 525	12 780	138	11 508	4 651

Note: all values in t/yr
* includes rock grinding and handling

16) Rivers and streams receiving fertilizer plant effluent usually have large enough flows to dilute the contaminants present to levels low enough to prevent any adverse environmental impact. However, in the area of the plant outfall (before mixing occurs) or, if the nitrogen, fluoride, etc. levels in the river upstream from the outfall are high, the additional loading from the plant could have an adverse environmental impact on the receiving body of water.

17) Short-term bioassays provide simple, fast, and relatively inexpensive means for detecting genotoxic activity in a variety of industrial effluent, raw water, and potable water sources. Periodic usage of such bioassays should be of value in identifying potential hazards and problem areas, monitoring the effectiveness of pollution control schemes, and setting priorities for in-depth and more specialized toxicological studies.

18) Genotoxicity test data based on short-term bioassays of a few effluent samples are inadequate for assessing possible hazards to human health and environmental effects. Whole-animal studies, possibly followed by epidemiological studies, would be required and even then it must be realized that, in the case of substances that have been shown to be carcinogenic in animals, toxicological extrapolation to humans in quantitative terms is difficult because data on dose/effect relationships, especially at low levels, are very limited.

19) Apart from the radiological studies advocated to study radioactive levels in seepages from gypsum ponds entering groundwater sources and radioactive emissions from phosphogypsum ponds and ways to decommission these ponds (which will also significantly lower fluoride emissions from these ponds), it is recommended that further regulatory initiatives by the federal government are not required at this time.

20) Fluoride, ammonia, SO_2, and NO_x emissions from this industry are of some concern; however, they are very small in comparison with other industrial sources. Thus, it is recommended that this industry be looked at again in 5 to 7 years.

1 INTRODUCTION

1.1 Background

Chemical fertilizers are compounded from a variety of chemicals containing one or more of the nutrient elements (nitrogen, phosphorus, and potassium). The fertilizer industry reviewed in this report includes the nitrogen and phosphate fertilizers but does not include potash-based fertilizers or mixed fertilizer plants.

The nitrogen fertilizer industry is considered to include the production of synthetic ammonia, ammonium nitrate, urea, ammonium sulphate, nitrogen solutions, and nitric acid as an adjunct process to that for ammonium nitrate. Production of all of these fertilizers often occurs at a single plant location.

The phosphate fertilizer industry, which converts insoluble phosphate rock into water soluble fertilizers rich in phosphorus, includes the production of phosphoric acid by the wet process (reaction of phosphate rock with sulphuric acid), the concentration of phosphoric acid, the production of normal and triple superphosphates, the manufacture of granular ammonium phosphates, and the production of sulphuric acid as an adjunct process to that for phosphoric acid. Phosphoric acid and superphosphoric acid serve as intermediates in the production of final fertilizer materials.

Fertilizer production rates in Canada are about five to six million tonnes per year. Of this amount, 80 to 85% are nitrogen-based fertilizers.

1.2 Objectives of the Study

During the production of nitrogen and phosphate fertilizers, as well as nitric and sulphuric acids, air emissions, water effluents, and solid residues are released into the environment. The objectives of this report were to review basic background information on the processes used in the fertilizer industry and on in-plant control of wastewaters produced, identify effluent sources, and establish the extent of toxic pollution discharges based upon information derived from chemical analyses and flow measurements of representative process wastewater effluents. In addition, emission points are identified, emission species are characterized, and average emission rates are determined. Solid waste residues are also characterized; however, except for the large amount of phosphogypsum produced during the production of phosphoric acid, solid residues released into the environment are relatively low for this industry.

Present and emerging control technologies are outlined in terms of their effectiveness, advantages/disadvantages, and extent of application.

1.3 General Approach and Methodology

The information included in this report was obtained from individual manufacturers through questionnaires and plant visits. Data on production capacities, wastewater characteristics, water pollution control measures, and air emission characteristics and control measures, as well as solid residue releases, were obtained in 1984/85 with assistance from the Canadian Fertilizer Institute. Some previous data, such as plant locations and monitoring, recording, and analytical test methods, as well as other miscellaneous information, which was collected through a questionnaire developed jointly by Environment Canada and the Canadian Fertilizer Institute in 1977/78, are also included.

A joint industry/Environment Canada (Conservation and Protection) screening survey was undertaken during the fall of 1980 and early 1981. Five plants, which should represent the entire cross section of the fertilizer industry, were included in the survey: one plant manufacturing only nitrogen fertilizer, one plant manufacturing only phosphate fertilizer, and three plants manufacturing both nitrogen and phosphate fertilizers. In general, five 24-hour composite samples were collected from each plant: three samples of final effluent, one sample of intake water, and one sample from another location, as suggested by plant personnel. All conventional parameters and toxic substances were analyzed in Environment Canada regional laboratories. Mutagenicity/carcinogenicity tests were carried out by the British Columbia Cancer Research Centre in Vancouver, B.C.

2 DESCRIPTION OF THE CANADIAN FERTILIZER INDUSTRY

2.1 Nitrogen Fertilizers

At present, the manufacture of nitrogen fertilizer is confined to the provinces of British Columbia, Alberta, Manitoba, and Ontario. The provincial environmental agencies have promulgated specific or general standards in line with the objectives of controlling pollutants responsible for air, water, and soil pollution. These effluent standards (Appendix Tables A1 and A2) are used as guidelines and stricter standards can be enforced if deemed necessary at specific plant sites.

Prior to the Second World War, relatively little anhydrous ammonia, or its derivatives, was manufactured in Canada. Two small plants in eastern Canada, operated by Canadian Industries Limited (CIL), jointly produced about 6000 t/yr, exclusively for refrigeration and other industrial purposes. Cominco Limited, at Trail, B.C., built the first sizeable plant in Canada, 35 000 t/yr, for use in the abatement of sulphur dioxide from the smelter. A number of coke plants in various parts of Canada produced ammonium sulphate, but on a very small scale.

In 1941, ammonia and ammonium nitrate plants were built at Calgary, Alta., and Trail, B.C., by Cominco Limited, and at Port Robinson, Ont., because of wartime requirements for explosives. It was not until the postwar period, however, that ammonium nitrate was available in quantity for the fertilizer trade. In the late 1950s, the direct application of ammonia to the soil and the use of nitrogen (urea/ammonium nitrate) solutions gained recognition in Canada as being important fertilizing techniques, and from then until the mid-1970s, production of all nitrogen fertilizers increased rapidly as a result of strong market demand and the availability of natural gas feedstock at a reasonable cost. As technology developed, so did plant capacities. Ammonia plants, commonly 100 to 300 t/d in the 1950s, increased in size to 1000 t/d and more in the 1960s and 1970s.

This review is concerned with the 12 plants producing nitrogen fertilizer products, three of which are located in Ontario, one each in Manitoba and British Columbia, and the remaining seven in Alberta (Figure 1). There are also three plants that manufacture ammonium nitrate prills for use in explosives and two small plants, operated by steel producers, that are mainly industrial outlets for ammonia. These five plants are not included in this review.

FIGURE 1 NITROGEN FERTILIZER PLANT LOCATIONS IN CANADA

Approximately 900 skilled personnel are employed directly in processing operations and another 2100 employees located at these plant sites are involved in other fertilizer related activities, such as maintenance, shipping, and laboratory work. These figures represent about 30% of the total number of employees in the fertilizer industry across Canada.

Production capacity of nitrogen fertilizer plants in Canada is shown in Table 1. The annual production capability of the Canadian nitrogen industry, given favourable market and operating conditions, is estimated to be as follows:

Anhydrous Ammonia	4 000 000 t
Ammonium Nitrate	1 000 000 t
Urea	2 500 000 t
Ammonium Sulphate	350 000 t
Nitric Acid	1 000 000 t

These estimates are based upon the total daily design capacities multiplied by the number of on-stream days that appears to be achievable by the plants (350 in the case of ammonia; 355 for the other products).

2.1.1 Anhydrous Ammonia. There are 12 plants in Canada producing anhydrous ammonia principally for the fertilizer industry, with daily production rates ranging from 180 to 2300 t/d (design capacity). Between 1950 and 1977, six producing units were closed down for various reasons, mainly because of size-related inefficiency. Plants built within the past few years have capacities ranging upward from 900 t/d and exceptional circumstances would have to prevail to justify smaller units. The replacement cost of existing capacity by today's standards would be well over one billion dollars.

Approximately 75% of Canada's annual output of ammonia is produced in Alberta, British Columbia, and Manitoba, with less than 5% of this output being used for nonfertilizer purposes. By contrast, approximately 22% of the ammonia produced in Ontario goes to industrial outlets. Overall, about 92% of total national production of this product is committed to agriculture in one form or another. Further expansion of ammonia capacity in Canada will depend upon a number of factors, such as market demand and the availability and cost of natural gas at competitive levels.

2.1.2 Ammonium Nitrate. Ammonium nitrate has been manufactured for many years as an ingredient for explosives, but it was not until this chemical was produced in prill form that it became generally available to the fertilizer industry. There are now

TABLE 1 PRODUCTION CAPACITY OF NITROGEN FERTILIZER PLANTS IN CANADA

Plant		Anhydrous Ammonia	Nitric Acid	Ammonium Nitrate	Urea	Ammonium Sulphate	Ammonium Solutions
A.	CIL, Courtright*	2 200	360	390	520	-	290
B.	Cyanamid of Canada, Niagara Falls	690	453	431	308	-	400
C.	Nitrochem Inc., Maitland	227	862	500	-	-	95
D.	Canadian Fertilizer, Medicine Hat	2 020	-	-	1 280	-	0
E.	Cominco, Calgary	300	75	100	200	-	4 (30% aqua ammonia) 128 (ammonium nitrate solution)
F.	Cominco, Carseland	1 200	-	-	1 600	-	0
G.	Cominco, Trail	191	-	-	-	410	400 (30% aqua ammonia) (captive use)
H.	Esso Chemical, Redwater	2 285	480	580	1 565	-	0
I.	Sherritt Gordon, Fort Saskatchewan	1 450	-	-	1 200	500	0
J.	Simplot Chemical, Brandon	575	300	360	400	-	500
K.	Western Co-op, Calgary	180	190	300	-	-	0
L.	Western Co-op, Medicine Hat	188	-	-	-	-	-
Total Canada		11 506	2 720	2 661	7 073	910	1 817

Note: all values in t/d

* 45 t/d of HNO_3 is concentrated; 280 t/d of NH_4NO_3 is prilled; 100 t/d of urea is sulphur coated

seven plants producing ammonium nitrate fertilizer in Canada: three in Ontario, one in Manitoba, and three in Alberta. Ammonium nitrate liquor is used in combination with urea liquor to provide nitrogen solutions that have become important sources of nitrogen in many areas.

Production capacities for ammonium nitrate in Ontario and western Canada are about equal, at close to 1400 t/d in each area, excluding production for the manufacturing of explosives. In Ontario, about 28% of the ammonium nitrate produced in fertilizer plants was sold for other uses, whereas in western Canada less than 5% went to industrial outlets.

Movement of ammonium nitrate from most plants in recent years was less than capacity due to unfavourable market conditions and also due to competition from urea, which has a significantly higher nitrogen content. It is probable that a new ammonium nitrate plant will not be built in Canada within the next 5 yr because of the competition from urea.

2.1.3 Urea. Urea, in prilled or granular form, is a relative newcomer to the Canadian fertilizer industry. There was no production until 1960, when plants were built in Ontario and Alberta. By 1975, production was just under 635 t/d in both Ontario (three plants) and western Canada (three plants). In 1976, two world-scale plants came on stream in Alberta, boosting production capacity by over 2450 t/d. More than 80% of Canada's urea production capacity is now located in Alberta and all but 1% is sold as fertilizer. By contrast, close to 20% of Ontario's production is used by other industries. (The Nitrochem urea plant closed in 1983.)

Urea, with its significantly higher nitrogen content compared with ammonium nitrate, has taken up the growth in the dry form nitrogen market and has also cut into markets formerly held by ammonium nitrate.

2.1.4 Ammonium Sulphate. Ammonium sulphate was the first solid nitrogen fertilizer manufactured in Canada, but the quantity available was relatively small, being limited to by-product tonnage from municipal gas plants and steel mill coking operations. In 1930, a plant was built in British Columbia that substantially increased the availability of ammonium sulphate in Canada, with significant quantities also being made available for the export market. In 1954, a plant was built in Alberta that, like the British Columbia operation, was built essentially for pollution control purposes rather than as a viable commercial venture. No new plants, with the exception of a small by-product plant in Ontario, have been built since 1954, the solid nitrogen market being served increasingly

by ammonium nitrate and urea, which have much higher percentages of nitrogen than ammonium sulphate.

2.1.5 Nitric Acid. Nitric acid, being an essential intermediate product, is manufactured at all plants in Canada engaged in the production of fertilizer-grade ammonium nitrate. A relatively small amount of nitric acid is sold, as such, for use in other industries.

2.1.6 Nitrogen Solutions. Most manufacturers having access to ammonium nitrate and urea liquors produce nitrogen solutions that are mixtures of these two products in proportions required to meet local requirements. Production is listed in this report and the constituent products have been accounted for. No manufacturing process is involved.

2.2 Phosphate Fertilizers

There are now seven plants in Canada producing phosphate fertilizers: one in New Brunswick, one in Manitoba (the plant in Manitoba imports phosphoric acid), three in Alberta, and two in British Columbia (Figure 2). Except for the plant in New Brunswick and one in British Columbia, all produce nitrogen fertilizers in addition to phosphate. Five of these plants were built and commenced operations from 1965 onward. The International Minerals and Chemical Corporation Ltd. plant in Port Maitland, Ontario, which used to produce sulphuric acid, phosphoric acid, ammonium phosphate, and normal and triple superphosphate, ceased operations early in 1984. The CIL Courtright plant, which used to produce phosphoric acid for the production of ammonium phosphate, ceased operations in 1986.

The raw material for the manufacture of phosphatic fertilizers is phosphate rock, which is imported from the U.S. About 1 360 000 t are imported from Florida and more than 1 000 000 t are imported from the western U.S. Sulphuric acid is manufactured on-site from Canadian sulphur at three locations and from smelter fumes for use at four locations (three of which are adjacent to the fertilizer operations). One plant imports phosphoric acid from its parent company in the U.S. All plants producing ammonium phosphates manufacture ammonia on the same site, except one, which draws from other company-owned locations. The chemical analysis of phosphate rock, as reported by Canadian fertilizer manufacturers, is shown in Table 2.

Based on 350 d operation, the total installed capacity for ammonium phosphates in Canada is close to 1 900 000 t/yr. All production is fertilizer grade. In eastern Canada, one producer manufactures and sells industrial quality phosphoric acid,

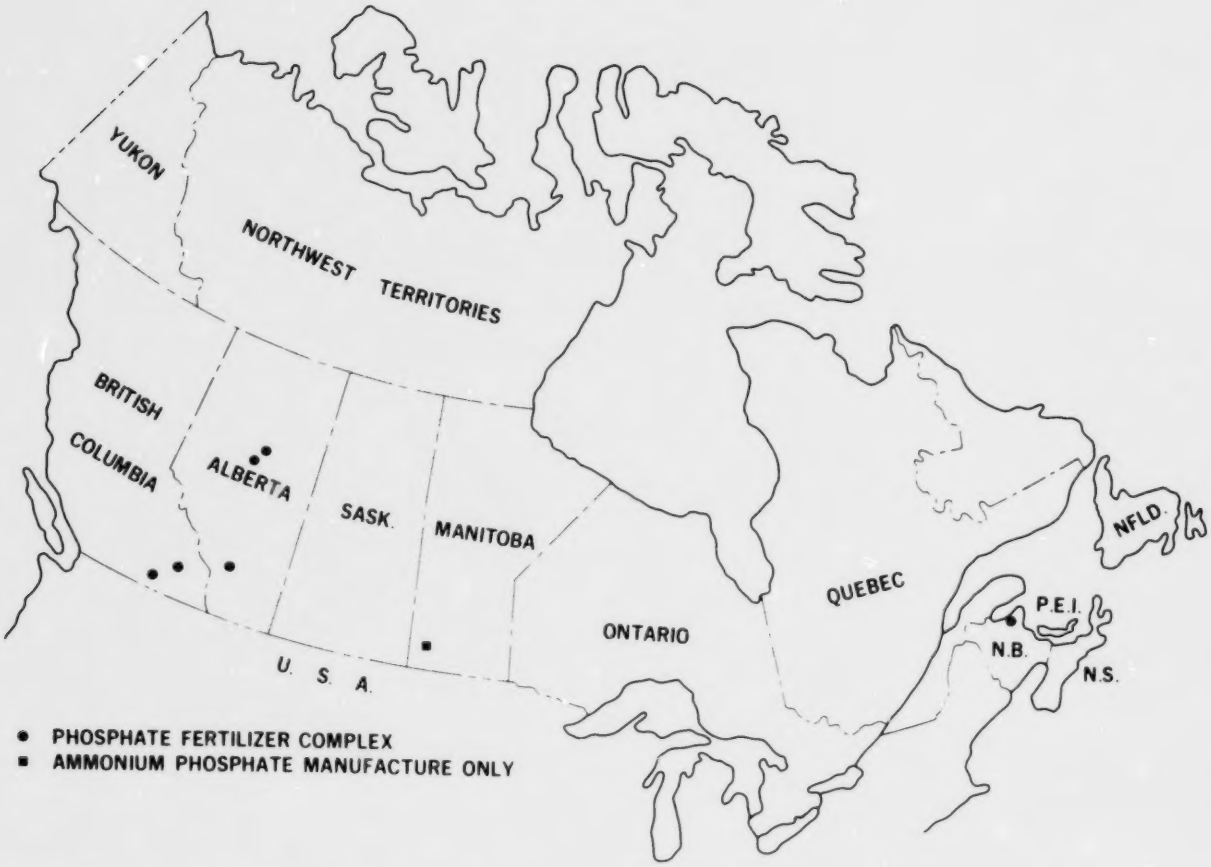


FIGURE 2 PHOSPHATE FERTILIZER PLANT LOCATIONS IN CANADA

but all other plants manufacture solely for fertilizer production. Production capacities of the Canadian plants are shown in Table 3.

Future expansion of phosphate fertilizer production will depend upon the delivered cost of phosphate rock to Canadian locations, the cost of natural gas for the production of ammonia, the cost of sulphur to those plants manufacturing sulphuric acid on-site, the environmental control costs, and, of course, the market demand. All of these costs must be weighed against those of the manufacturers in the U.S. who, by and large, are situated at the source of phosphate rock and have a distinct advantage over most Canadian producers because of their proximity to saltwater ports. In general terms, the Canadian industry is likely to be a predominantly domestic supplier, with relatively little opportunity for significant exports.

TABLE 2 CHEMICAL ANALYSIS OF PHOSPHATE ROCK AS REPORTED BY CANADIAN FERTILIZER MANUFACTURERS

Chemical Constituent	Florida	Utah, Idaho, Montana
Silica or insoluble SiO_2	7.1-9.6	9.8-17.9
Fluoride (F)	3.3-3.9	3.3-3.8
P_2O_5	31.0-32.98	30.3-33.0
As_2O_3	0.001-0.0018	0.001-0.008
CdO	0.0008-0.001	0.0002-0.0003
U_2O_3	0.006-0.05	0.004-0.07
V_2O_5	0.008-0.086	0.006-0.12
Hg	0.00001	0.0001
MgO	0.36	0.5
CaO	48.5	-
Al_2O_3	0.84-0.93	1.2
Fe_2O_3	0.99-1.22	1.1
Zn	0.004	-
Pb	0.002	-
Cu	0.0013	-
NaO	0.048	-
K_2O	0.08	-

Note: all values are percentages by weight

Approximately 550 people are engaged directly in the manufacture of basic phosphatic fertilizers in Canada, including about 50 who are employed in the operation of on-site sulphuric acid plants.

2.2.1 Ammonium Phosphate. The first two ammonium phosphate plants in Canada were built in British Columbia in 1931 and 1953. A plant was built in Alberta in 1956, but there was no further construction until the 1960s, and from 1961 to 1969, seven new plants came on stream in Canada: three in eastern Canada (two of which are now closed) and four in western Canada (one of which is temporarily closed). These plants produce several grades of ammonium phosphate, such as 11-48-0, 11-55-0, 11-51-0, 13-52-0, and

TABLE 3 PRODUCTION CAPACITY OF PHOSPHATE FERTILIZER PLANTS IN CANADA

Plant		Phosphoric Acid (as P_2O_5)	Sulphuric Acid	Ammonium Phosphate	Phosphate Solutions
A.	CIL*	170	-	330	-
G.	Cominco, Trail	222	1200	600	-
H.	Esso Chemical	840	1800	2000	-
I.	Sherritt Gordon	220	640	480	-
J.	Simplot Chemical	***	-	-	250
K.	Western Co-op, Calgary	590	1300	1090	-
L.	Western Co-op, Medicine Hat**	-	-	-	-
M.	Cominco, Kimberley	250	900	450	-
N.	Belledune Fertilizer	400	-	800	-
Total		2692	5840	5750	250

Note: all values in t/d
* this plant ceased operations in 1986
** this plant is presently not producing phosphate fertilizers
*** purchased from associated source

18-46-0. The popularity of ammonium phosphate, when compared with triple superphosphate, relates to the fact that, although the latter contains 46% P_2O_5 plus substantial amounts of nitrogen, freight and handling costs are obviously reduced on a total plant food basis and storage requirements for other forms of nitrogen, such as urea and ammonium nitrate, are minimized.

2.2.2 Phosphoric Acid. All phosphate plants, except the plant in Manitoba, produce phosphoric acid.

3 PROCESS DESCRIPTION

3.1 Nitrogen Fertilizer Production Processes

3.1.1 Anhydrous Ammonia.

Catalytic steam reforming of natural gas. Most of the ammonia produced in Canada is by catalytic steam reforming of natural gas (Figure 3). Ammonia production basically involves the following seven processes for production of hydrogen, synthesis gas purification, and ammonia synthesis:

1) feedstock desulphurization,
2) primary reformation,
3) secondary reformation,
4) high and low temperature CO shifts,
5) CO_2 absorption,
6) methanation, and
7) ammonia synthesis.

Feedstock desulphurization. Natural gas contains sulphur compounds, mostly hydrogen sulphide and carbonyl sulphide, which must be reduced to as low a level as is economically possible to prevent poisoning of the nickel catalyst in the primary reformer. To achieve this, producers use activated carbon beds with a metallic additive or zinc oxide beds or a combination of the two to remove sulphur compounds from the feedstock.

Primary reformation. In the primary reformer, the desulphurized natural gas is mixed with steam, in the presence of a catalyst, to convert methane to carbon monoxide and hydrogen.

$$CH_4 + H_2O \xrightarrow{550°C} CO + 3H_2$$

The reaction is endothermic and requires the input of a large amount of heat. The heat required for the reforming step is supplied by firing natural gas, and in some cases purge gas, in the radiant heat section of the primary reformers. Roughly 65 to 75% conversion takes place.

Secondary reformation. The process gas passes into the secondary reformer where it is mixed with compressed air preheated to 550°C, to give a hydrogen to nitrogen mole ratio of 3:1. The heat necessary for completion of the reforming reaction is supplied by combustion of the two gases as they mix in the reformer. Gas temperature at the exit

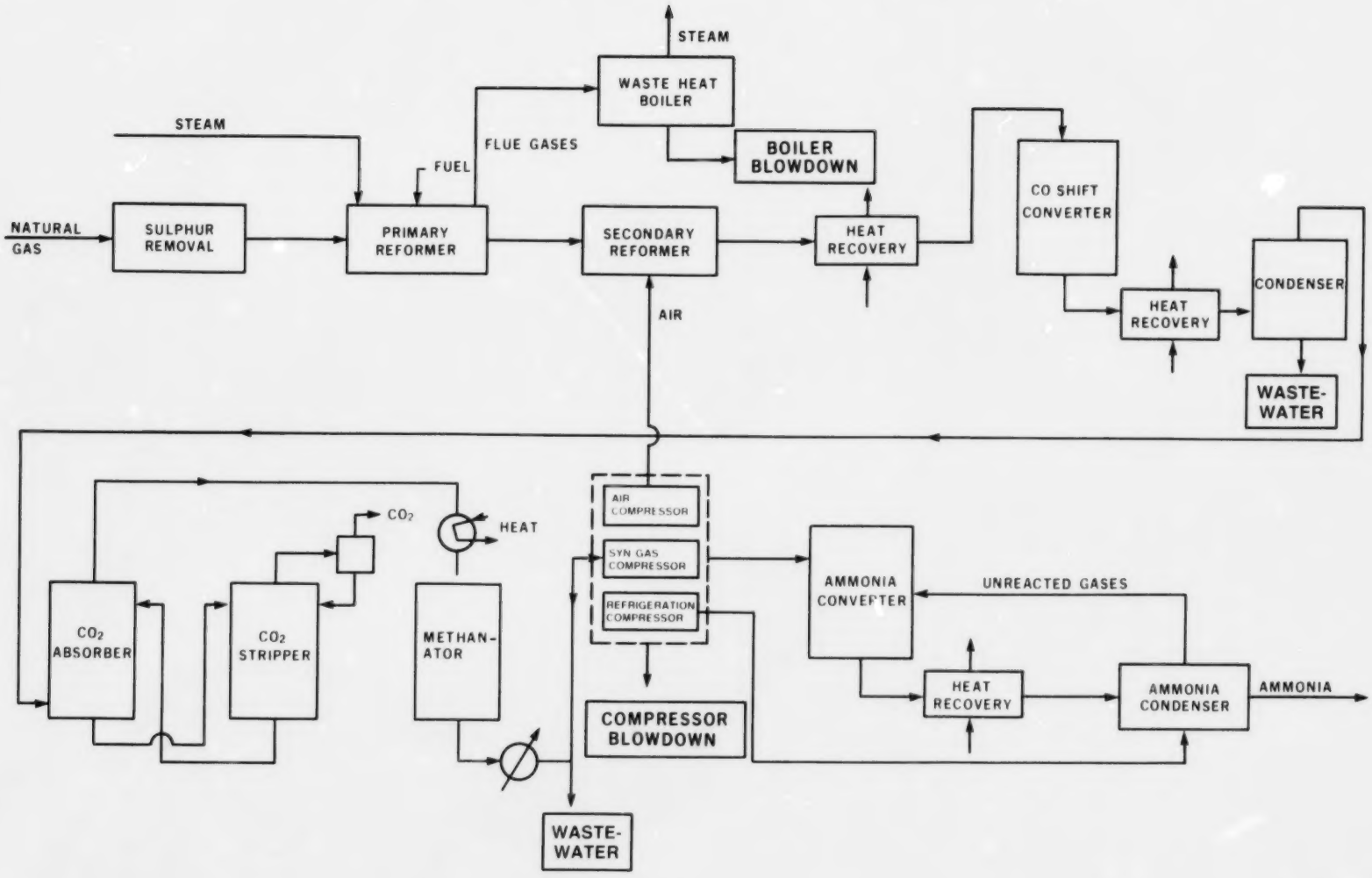


FIGURE 3 PROCESS FLOW SHEET - AMMONIA PRODUCTION

of the secondary reformer, at around 950°C, is reduced to approximately 350°C in a waste heat boiler.

High and low temperature carbon monoxide shifts. Cooled gas from the secondary reformer, which has passed through the waste heat boiler, enters the high temperature CO shift converter, which is filled with a chromium oxide - iron oxide shift catalyst, to convert the CO to CO_2.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The shift gas is cooled in a heat exchanger and passes into the low temperature shift converter to further carbon monoxide removal. Unreacted steam, which was added in the primary reformer (an excess is needed) is condensed and the condensate separated. Most of the process wastewater from ammonia production comes from this process condensate.

Carbon dioxide absorption. Carbon dioxide must be removed from the shift gas because it poisons the ammonia synthesis catalyst. Most ammonia producers remove the CO_2 from the shift gas by a monoethanolamine scrubbing system, by a hot carbonate scrubbing system, or by a Sulfinol scrubbing system. The scrubbing materials are regenerated by steam stripping.

Methanation. After the CO_2 absorption towers, the synthesis gas still contains very low concentrations of carbon dioxide, which must be removed because they poison most ammonia synthesis catalysts. The residual CO_2 is removed by catalytic methanation according to the following reactions:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Condensate is removed from the synthesis gas in a knockout drum. The synthesis gas now has a 3:1 mole ratio of H_2:N_2 and contains less than 1% methane and argon.

Ammonia synthesis. Anhydrous ammonia is synthesized directly in two stages: first by compression and then by passing the purified gas over a catalyst at elevated temperature and pressure. Fresh synthesis gas from the methanator is compressed and mixed with recycled synthesis gas and then cooled. Condensed ammonia is separated and sent to a let-down separator. The unconverted gas is compressed and preheated before

entering the converter. Gas from the converter is cooled and the condensed ammonia is separated, let down in pressure, and stored in tanks. A small portion of the overhead gas is purged to prevent the buildup of inerts.

Partial oxidation. The partial oxidation process can be used for feedstocks ranging from natural gas to heavy fuel oils; thus, this process can be used where natural gas is unavailable. At the Nitrochem plant in Brockville, natural gas is used; however, this process does require a source of oxygen and nitrogen, which is normally obtained from a liquid air plant.

Air separation. The function of the air separator is to liquify and separate air, drawn in from the atmosphere, into nitrogen and oxygen. The air separation units are called cryogenic units because they operate at subzero temperatures, which is required because air will not liquify at normal atmospheric pressure until a temperature of -193°C is attained.

Air, which is drawn in by compressors, contains small amounts of water vapour and CO_2. These two components of air must be removed from the high pressure air before it enters the cold box or they will freeze and block the lines. Carbon dioxide is removed by liquid absorption using a dilute caustic solution in a tower, and water vapour is removed when the air passes through an air dryer. The pressure is raised to around 18 000 kPa before the high pressure air enters the cold box where it is subcooled and liquified. When the liquid air is subjected to a lower pressure, the nitrogen vaporizes from the oxygen and separation of the two major components of air is accomplished. The nitrogen leaving the cold box contains a maximum of 40 ppm oxygen. The oxygen is usually around 90%, with mostly nitrogen and some argon making up the balance.

Hydrogen generation. Methane gas is fed to a Texaco hydrogen generator where it reacts with oxygen from the air plant. The reaction of the natural gas and oxygen is referred to as the partial oxidation of natural gas, which takes place at a reaction temperature of approximately 1315°C and an operating pressure of 2800 kPa. The overall reaction may be written as

$$CH_4 + 1/2\ O_2 \rightarrow 2H_2 + CO$$

Demineralized water is added to cool the gas, reduce carbon formation, and increase the amount of hydrogen in the combustion gases. In spite of the addition of steam, one of the smaller reactions in the generator is the cracking of methane into carbon and hydrogen. Most of the carbon is removed by a blowdown from the bottom of

the generator and any remaining carbon is removed by scrubbing with condensate in carbon scrubbers, through which the gas passes on leaving the generator. This step is essential as carbon would deactivate the catalyst in the CO converters.

CO conversion. The gas, now free of carbon particles, passes into a high temperature carbon monoxide converter where most of the CO is converted to carbon dioxide. This reaction may be written as

$$CO + H_2O \rightarrow CO_2 + H_2 + \text{heat}$$

The gas now passes into a low temperature converter where most of the remaining CO is converted to carbon dioxide. Because there is no longer any need for the gas to be saturated with steam, the temperature is lowered further in a water scrubber, causing much of the water to condense out of the gas. This water is recycled to the generator and high temperature converter.

Carbon dioxide stripping. The gas stream now flows into the first of two CO_2 removal systems. The potassium carbonate system absorbs the bulk of the carbon dioxide and is followed by a monoethanolamine system that absorbs the remaining carbon dioxide.

Each carbon dioxide removal system has a regenerating system whereby the bicarbonates are boiled, releasing carbon dioxide from solution so that it may be used again for absorption purposes. The CO_2 may go to the urea plant if it is operational, to a customer, or to the atmosphere.

The carbonate and monoethanolamine (MEA) absorption and regeneration steps may be written as

Carbonate absorption	$K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3$
Carbonate regeneration	$2KHCO_3 + \text{heat} \rightarrow K_2CO_3 + H_2O + CO_2$
MEA absorption	$2C_2H_5ONH_2 + CO_2 + H_2O \rightarrow (C_2H_5ONH_2)_2 + H_2CO_3$
MEA regeneration	$(C_2H_5ONH_2)_2 + H_2CO_3 \rightarrow 2C_2H_5ONH_2 + H_2O + CO_2$

Nitrogen scrubbing units. The hydrogen gas leaving the CO converters still contains very small quantities of unreacted carbon monoxide, methane, and argon, which must be removed. One way of removing these impurities is by scrubbing the gas stream with liquid nitrogen. The process operates at subzero temperatures; thus, any moisture or carbon dioxide must be removed from the hydrogen stream prior to entering the nitrogen scrubbing units. Therefore, the hydrogen gas is passed through a CO_2 removal tower followed by a dryer system to remove any carbon dioxide and water remaining in the gas.

The dry, carbon-dioxide free, hydrogen gas is scrubbed with liquid nitrogen, which comes from the air separation plant. The liquid nitrogen is cold enough to cause the carbon monoxide, methane, and argon to liquify from the hydrogen gas stream, yet not cold enough to cause the hydrogen to liquify. The impurities are carried out of the scrubbing towers with the residual nitrogen, which is vaporized and used in the gas drying unit. Nitrogen is added to the pure hydrogen leaving the nitrogen scrubbing units to bring about the proper hydrogen-nitrogen molar ratio of 3:1. This is synthesis or syn gas.

Ammonia synthesis. The bonding of the two gases is very difficult and must be subjected to a pressure of 20 000 to 33 000 kPa and a temperature of 515°C over a catalyst; still, only about 20% conversion is attained. The gas leaving the converter is cooled, causing the 20% ammonia formed to liquify. The stream is then fed to a separator where the liquid and gas are separated. The unreacted gas flows back and is mixed with the syn gas before it once more passes over the ammonia catalyst. The product, liquid ammonia, is let down in pressure and sent to spheres for storage.

3.1.2 Ammonium Nitrate. All, or almost all, ammonium nitrate produced in Canada is based on the reaction of ammonia with nitric acid (Figure 4).

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

The reaction between nitric acid and ammonia is carried out in a reactor or neutralizer. A 55 to 60% nitric acid stream is used in the reaction to produce a 61 to 65% ammonium nitrate solution. The heat generated in this reaction is used to drive off a portion of the remaining water, further concentrating the solution to 73 to 83% ammonium nitrate.

During neutralization, the lower the pH, the lower the ammonia losses will be. Reaction pH is usually held in the 4 to 5 range. Under normal operating conditions, the neutralizer temperature is maintained at around 130°C either by adding a weak ammonium nitrate recycle liquor (the oversize and undersize from the screening of the prill tower product is dissolved in a tank) or by varying the nitric acid feed strength. To minimize ammonium nitrate decomposition, the maximum temperature permitted is about 148°C.

The 73 to 83% ammonium nitrate solution from the neutralizer is concentrated further using a falling film or two-stage evaporator with a steam-jet ejector and/or barometric condenser. This step yields a 95 to 97.5% melt for low density production or a 99.5% melt for high density prill production and granulation.

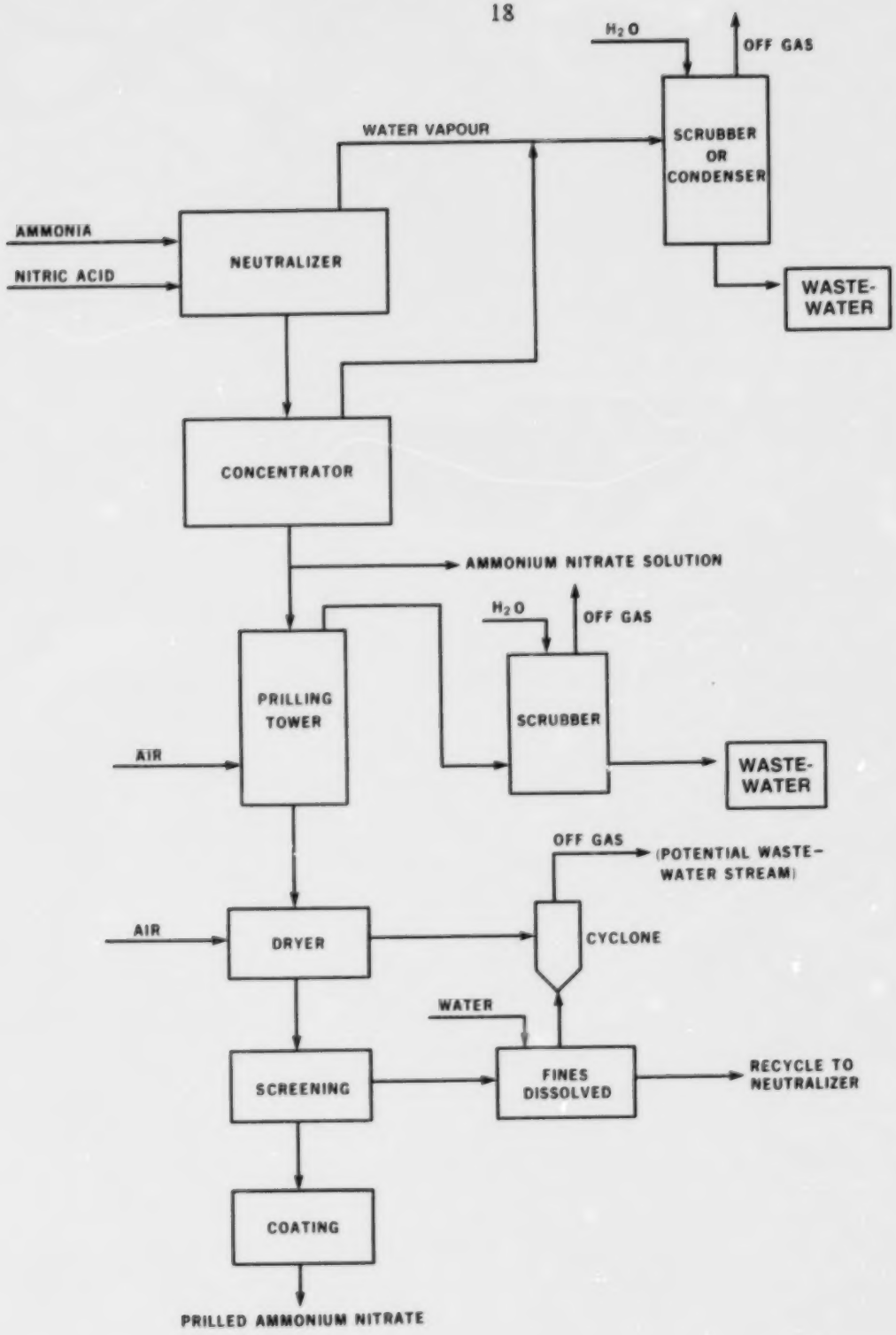


FIGURE 4 PROCESS FLOW SHEET - AMMONIUM NITRATE PRODUCTION

Particle formation is generally accomplished by prilling, drum granulation, or crystallization. If a prilled product is desired, the solution from the concentrator is pumped to a head tank in the top of a high tower and sprayed down into a rising current of heated air. The airflow cools the falling droplets and allows their surfaces to crystallize before reaching the bottom of the tower. The solid prills are either carried away on a conveyor belt or are fluidized by the air entering the tower, which allows the prills to cool further, with minimum caking, before being removed.

If drum granulators are used, a pipe running axially near the centre of the granulating section emits a fine spray of ammonium nitrate (AN) melt onto fine seed particles, which enter at the feed end of the granulator. As the particles pass through the spray, they are coated with molten AN, which cools and hardens on the particles as the lifting flights carry them away. This process is repeated, with the particles gradually building up to product size, through the addition of successive layers, before they overflow the dam and enter the cooling section of the drum. Granulators require less air than prill towers. The airflow, which is generally cooled before entering the granulator, removes the heat of crystallization of the ammonium nitrate and can entrain up to 10 to 20% by weight of product.

When crystalline ammonium nitrate is desired, the solution from the concentrator is fed into a continuous crystallizer. In the crystallizer, the solution is cooled by vacuum evaporation to produce crystals of AN. The crystals are withdrawn from the crystallizer and sent to a continuous centrifuge where the crystals and liquor are separated. The liquor from the centrifuge is recycled to the crystallizer. The crystals are passed to a dryer.

The ammonium nitrate industry utilizes various combinations of finishing equipment to cool, dry, screen, and coat AN solids depending on the formation process. High density prills are cooled, screened, and sometimes coated; low density prills are predried, dried, cooled, screened, and coated; drum granulated product is screened, cooled, and may be coated; and crystalline AN is dried, cooled, screened, and coated.

Typically, drying is performed by two rotary drum dryers in series, although fluidized bed coolers could gain some acceptance. It is common practice to use a coating or additive to prolong shelf life and to suppress dust emissions of solid AN particles. Additives include calcium oxide, magnesium oxide, magnesium nitrate, diatomaceous earth, and fatty amine-clay mixtures.

In most plants, it is common for the material to be transported by conveyor belt from one process to the next. Ammonium nitrate is shipped mainly in bulk form.

3.1.3 Urea. Urea is produced by reacting ammonia and carbon dioxide to form ammonium carbamate (Figure 5).

$$2NH_3 + CO_2 \rightarrow NH_4CO_2NH_2$$
$$NH_4CO_2NH_2 \rightarrow NH_2CONH_2 + H_2O$$

The carbamate is then dehydrated to yield urea. The overall urea manufacturing process can be broken down into solution formation and concentration, solids formation and cooling, and product finishing and handling.

Solution formation and concentration. The formation of urea is dependent upon temperature, pressure, and concentrations of ammonia, carbon dioxide, water, urea, and carbamate. Experiments have shown that the yield can be improved by raising the temperature and pressure and by changing the molar ratio. Excess water affects the equilibrium yield by reducing the unit's productive capacity and increasing the quantity of water to be evaporated, thus consuming more energy.

There are basically three methods of producing urea: (1) once-through processes, (2) partial recycle processes, and (3) total recycle processes. By far the most important class from an environmental point of view is the total recycle process.

Total recycle processes. The three variations in the total recycle process are (1) recycling, in their pure state, of the separated decomposed carbamate gases; (2) recycling of the carbamate solution to the reactor; and (3) recycling of a combination gas/liquid solution. A number of companies have incorporated at least one of these categories in their designs, e.g., the CPI-Allied and Inventa processes recycle the gases; the Stamicarbon, Montecatini, Pechiney, and Inventa processes recycle the carbamate solution; and the Mitsui Toatsu, Stamicarbon, SNAM PROGETTI, Chemico, and Lonza-Lummus processes recycle ammonia, with carbon dioxide being recycled in the form of carbamate.

Montedison reports that they have an updated process (isobaric double recycle) that cuts energy consumption by 40%. The conversion of CO_2 to urea has been boosted from 60% to 70% by using large excesses of ammonia. Recycling is achieved via two separate decomposers in series. In the course of decomposing and recycling carbamate, about 90% of the ammonia and 45% of the carbamate contained in the urea solution are removed and recycled (1).

Mitsui Toatsu has announced details of an improved process (advanced process for cost and energy) that it developed with Toye Engineering Corp. The new process

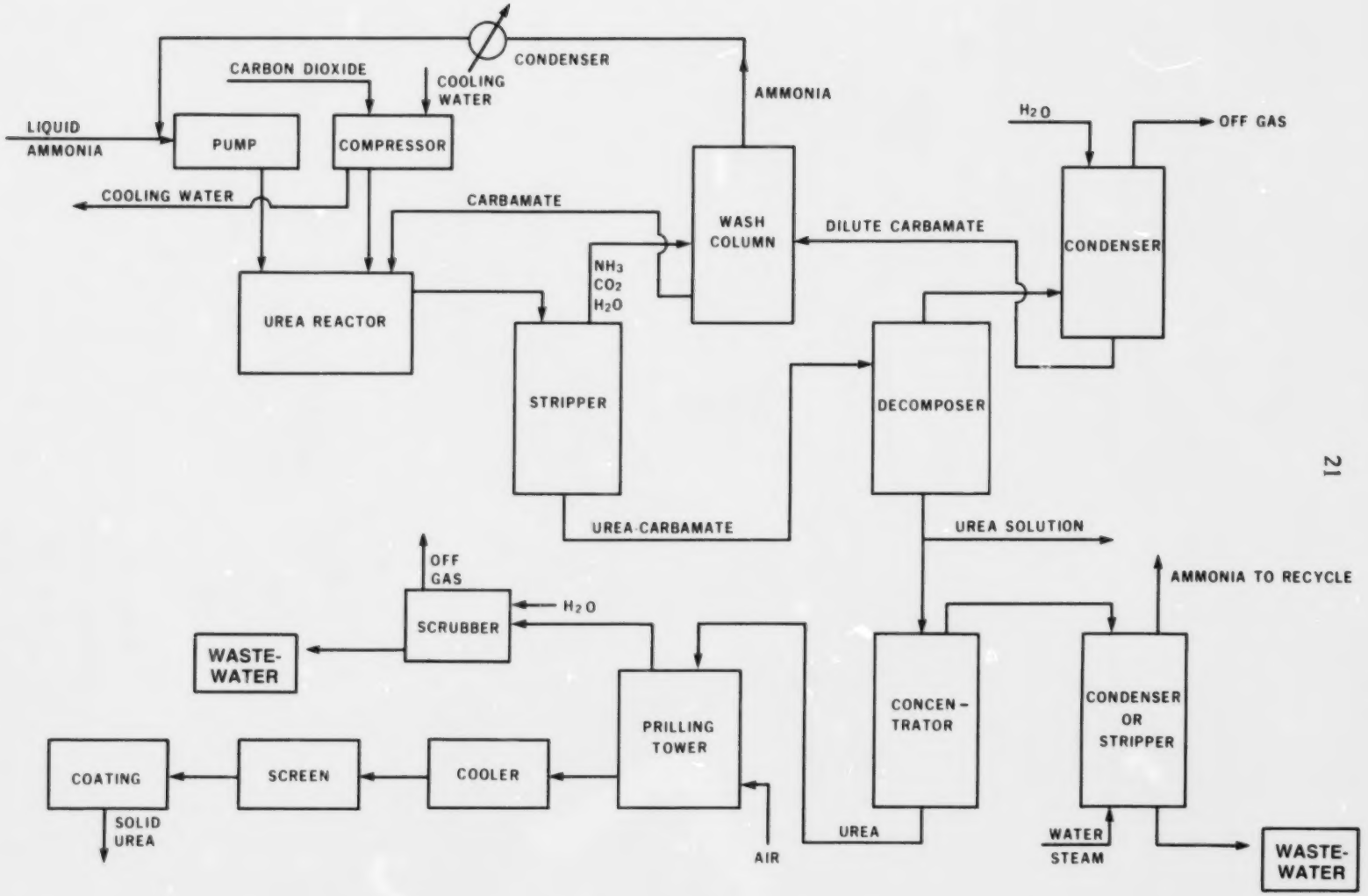


FIGURE 5 PROCESS FLOW SHEET - UREA PRODUCTION

involves the addition of a stripper after the urea reactor, which cuts down on the volume of flow (and thus energy consumption) in downstream vessels. The stripped carbamate and ammonia are sent to a carbamate condenser to be separated and eventually recycled to the reactor. In addition, the reactor, stripper, and condenser are all operated at the same pressure, which allows for more high-quality steam recovery. These modifications reportedly cut overall energy consumption by 40% relative to the "total recycle C-improved urea process" (2).

Irrespective of the solution formation process, the two methods of concentrating urea solution prior to solid formation are crystallization and evaporation. The method chosen depends on the acceptable biuret ($NH_2CONHCONH_2$) level, an impurity formed by a side reaction. To obtain urea with less than 0.4% biuret, crystallization is necessary. A vacuum crystallizer evaporates water using the sensible heat of the urea solution and the heat of crystallization. The crystallizer slurry, containing urea crystals, is centrifuged. The solids are separated, washed, and dried. The crystals are then melted and sprayed into the solidification device. A thin-film evaporator, which can be controlled at around 130°C, is normally used.

Solids formation and cooling. The formation of solid urea requires a critical balance between temperature, retention time, and airflow due to its heat of crystallization, melting point, and decomposition properties. Solid product can be formed by essentially three methods: prill towers, drum and pan granulators, and crystallization. As already noted, crystallizers are used to concentrate the urea solution. The crystallizer slurry, containing around 30% solids, is centrifuged and the separated solids are washed and dried. These solids can be screened and coated as a final product or melted and sprayed into one of the following solidification devices.

In the prilling process, concentrated urea solution is pumped to the top of a 30 to 35 m tower and forced through a spraying device. The urea droplets fall countercurrent to an airflow. The airflow cools the falling droplets and allows the droplets to crystallize before reaching the bottom of the tower, where they are removed.

In the granulation process, the urea melt enters a granulation drum through a spray bar, which distributes the melt on a tumbling bed of particles. Particles of appropriate size exit the drum by passing over a retaining dam.

In the pan granulator, the circular pan rotates and is tilted. Feed material deposited at the top falls through a fine spray of liquid urea and the larger granules spill over the edge of the tilted pan onto a conveyor belt and into a rotary cooler.

Product finishing and handling. The final preparation consists of cooling, screening, and coating. Oversized and undersized material is recycled. Very little of the solid urea produced is coated because the practice of injecting formaldehyde or phosphate-based additives into the melt prior to solid formation has increased. The structures and quantities of the phosphate-based additives and formaldehyde are proprietary. When diatomaceous earth or kaolin are added to the particles, the quantities usually vary from 0.3 to 2.0%. This coating process occurs in a large warehouse and requires no external vents.

3.1.4 Ammonium Sulphate. Ammonium sulphate is an ammonium salt of sulphuric acid containing 21.2% nitrogen, with fertilizer grades averaging 20 to 21% nitrogen. It is manufactured in Canada in several ways, the most important being absorption of ammonia in sulphuric acid (Figure 6).

The reaction is carried out in a crystallizer reactor and the ammonium sulphate formed is recirculated as a slurry. The reaction is exothermic and the heat generated facilitates both water evaporation and precipitation of the salt. The ammonium sulphate slurry is then sent to a centrifuge to remove the mother liquor for recycling back to process. The crystal cake formed goes to a gas-fired dryer to form ammonium sulphate crystals with less than 0.1% moisture content.

3.1.5 Nitric Acid. Nitric acid is produced in Canada by the high temperature catalytic oxidation of ammonia process (Figure 7). The main components of an ammonia oxidation nitric acid plant are the (1) converter section, where the ammonia vapour and air are mixed and reacted catalytically to oxidize the ammonia; (2) cooler-condenser section, where the nitrogen dioxide is produced by cooling the reaction gases and weak nitric acid is formed; (3) absorber section, where the cool nitrogen dioxide is absorbed in water to form nitric acid; and (4) emission control equipment.

In the first step, one volume of anhydrous ammonia is mixed with nine volumes of compressed, filtered air and passed through a multilayered platinum-rhodium catalyst at about 900°C. Under these conditions, the oxidation of ammonia to nitric oxide proceeds according to Equation 1. The reaction is exothermic and is about 95% complete under these conditions.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (1)$$

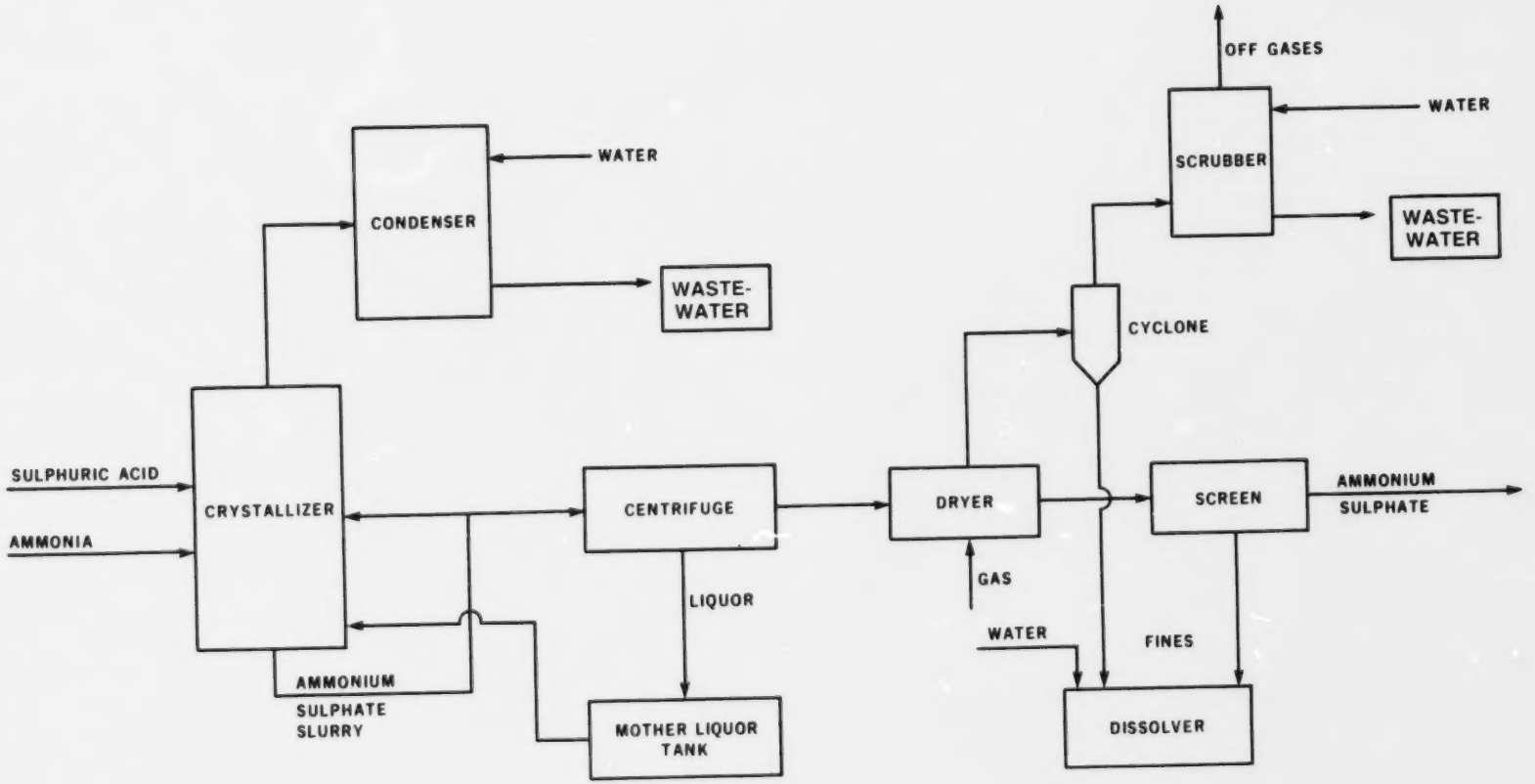


FIGURE 6 PROCESS FLOW SHEET - AMMONIUM SULPHATE PRODUCTION

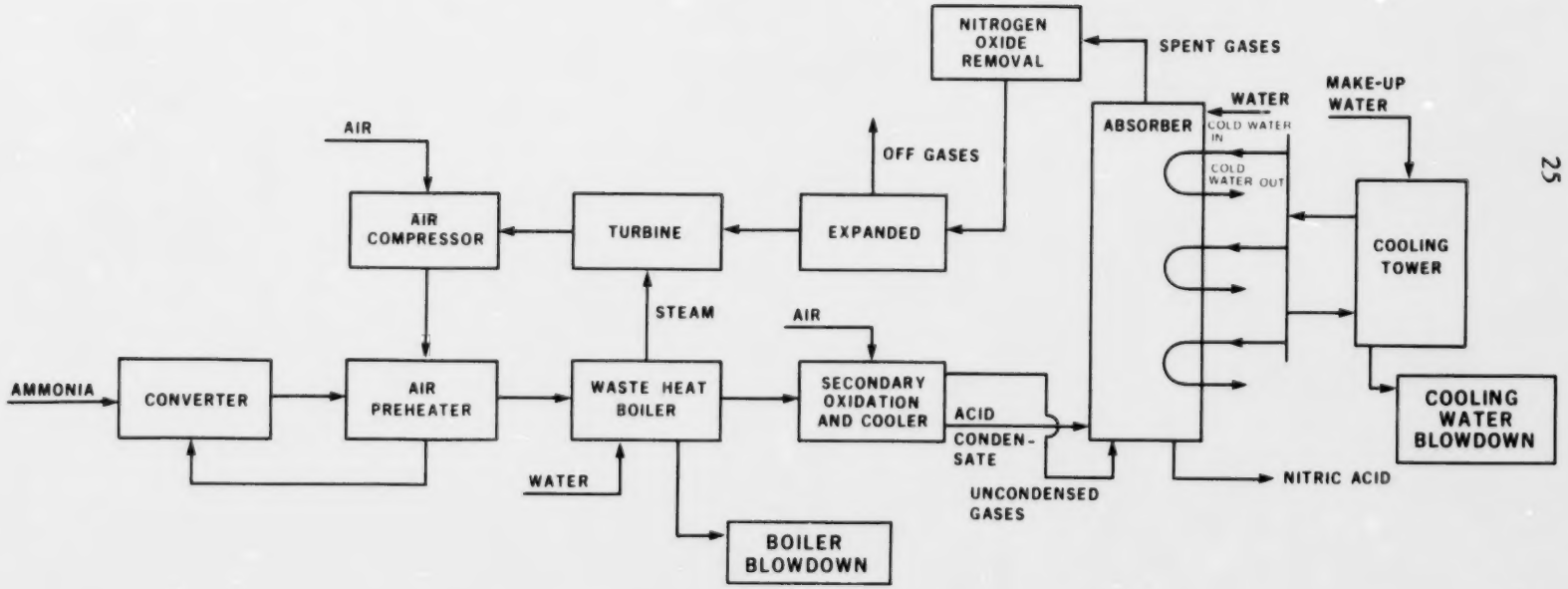


FIGURE 7 PROCESS FLOW SHEET - NITRIC ACID PRODUCTION

The second step involves the oxidation of the nitric oxide to nitrogen dioxide, as shown in Equation 2.

$$2NO + O_2 \rightarrow 2NO_2 \rightarrow N_2O_4 \qquad (2)$$

The forward rate of this reaction is favoured at lower temperatures and higher pressures.

The process gas from the reactor passes through a heat exchanger, the first part of which is the burner gas boiler, which produces steam, followed by a platinum recovery filter. The gas then passes through a cooler, where the gas temperature is reduced, allowing some of the acid formed to condense. This weak acid solution is removed from the gas stream in an acid separator and is sent to the midsection of the absorption tower.

In the third step, the process gas is passed to an absorber where it reacts with water to produce an aqueous solution of 50 to 60% nitric acid, the concentration depending on the temperature, pressure, number of absorption stages, and concentration of the NO_2 entering the absorber. The equation may be written as

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (3)$$

The formation of nitric acid in Equation (3) involves the disproportionation of nitrogen dioxide to form two moles of HNO_3 for every mole of NO. To reoxidize the nitric oxide during absorption, secondary air (also known as bleacher air) is introduced into the absorber along with the nitrogen dioxide. The acid product is withdrawn from the bottom of the tower. The air entering the bottom of the tower serves to strip NO_2 from the product and to supply oxygen for reoxidizing the NO formed in making nitric acid.

The oxidation and absorption operations are carried out at high, medium, and low pressures. Both operations can be carried out at the same pressure or at different pressures.

In the high-pressure process, the oxidation of ammonia and the absorption of the resulting nitrogen oxides are both carried out at around 530 to 800 kPa. Acid strengths of 60% are normal.

In the intermediate-pressure process, the plant operates at pressures of 130 to 400 kPa throughout the plant. The basic process is the same as the high-pressure system, except that additional absorber volume is required.

In the low-pressure process, which has become outmoded, the basic chemistry of the process is identical to that of the high-pressure process, except that all reactions occur at essentially atmospheric pressure. Because of the poor absorption characteristics

of NO_2 in water at atmospheric pressure and the very slow rate of reoxidation of NO to NO_2, a large absorption volume is required. This is because the rate of oxidation of NO to NO_2 varies directly with the square of the pressure, and operation at atmospheric pressure thus requires greatly increased time for oxidation to occur. Acid strengths ranging from 40 to 50% are normal.

As mentioned above, oxidation and absorption processes can operate at different pressures. In the dual pressure process, moderate pressure oxidation and high pressure absorption are employed.

Ammonia, vaporized by steam, is heated and mixed with air from the compressor at 300 to 500 kPa. The ammonia/air mixture is catalytically oxidized in the reactor and the heat is recovered in a waste heat boiler. The gases are further cooled by a tail gas heat exchanger and water cooling before compression to the absorber pressure of 800 to 1400 kPa. Nitric acid of up to 70% concentration is collected. High yields of up to 96% conversion can be obtained using this process.

The final step is the control of NO_x emissions, which are inevitably present in the waste gas discharged from the absorption tower irrespective of the process used. This topic will be discussed further in another section.

3.2 Phosphate Fertilizer Production Processes

The phosphate fertilizer industry consists of four basic plants: phosphoric acid, normal superphosphate, triple superphosphate, and ammonium phosphate. Because of the large amount of sulphuric acid consumed by this industry, many of the plants provide for their own acid needs.

3.2.1 Phosphate-Rock Grinding. Beneficiated phosphate rock requires additional processing to reduce the ore to the size range for optimal phosphoric acid production. Grinding is normally carried out in ball mills; however, rod mills and hammer mills may be used.

After the rock enters the mill, flow-through sizing and reclamation are accomplished by pneumatic means, when dry grinding is performed. Air is constantly exhausted from the system and is vented to the atmosphere via a bag filter, which removes entrained rock particles. This fine dust is recycled to the system.

An alternative to dry grinding is wet grinding. Wet grinding reduces energy requirements by eliminating drying of the rock, eliminates the need for dry storage, and greatly reduces problems in the collecting and handling of dust. Wet grinding is accomplished through the addition of small amounts of water to the feed; thus, the

flow of ground rock is in the form of a slurry. The water added to phosphate rock for wet grinding is incorporated into the process reactants. No wastewater effluents are produced by either dry or wet grinding.

3.2.2 Phosphoric Acid. Phosphoric acid is produced by the decomposition or acidulation of phosphate rock, the most common rock being fluorapatite ($Ca_3(PO_4)_2CaF_2$), containing 3 to 4% fluorine. Any strong mineral acid can be used for acidulation; however, sulphuric, nitric, or hydrochloric acid are most commonly used.

In this method, termed the "wet process," finely ground phosphate rock is digested with 55 to 70% sulphuric acid, resulting in the emission of significant quantities of gaseous fluorides (Figure 8). The overall reaction is described by the following equation:

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2 + 58H_2O \rightarrow 30CaSO_4 \cdot 2H_2O + 18H_3PO_4 + H_2SiF_6$$

Calcium sulphate precipitates and the liquid phosphoric acid is separated by filtration. The reactor is constructed to provide sufficient retention time for gypsum crystal growth and to prevent short-circuiting of the rock. This reaction is exothermic and, thus, requires some cooling. In addition to this main reaction, several side reactions take place due to the large amount of impurities in the rock. In some rocks, additional fluorine is present in the form of calcium fluoride. This is acid attacked to form gypsum and hydrogen fluoride. Hydrogen fluoride then reacts with the silica in the rock to give silicon tetrafluoride (SiF_4), which hydrolyzes to form fluosilicic acid (H_2SiF_6). At higher temperatures, this acid decomposes to release gaseous silicon tetrafluoride and hydrogen fluoride. Depending on the impurities in the rock, several other minor reactions can occur to release gases and solids.

Digester reaction time generally varies from 3 to 8 hours, with the temperature being maintained at 80°C. The acidulation requirements are 2.6 t of 100% acid per tonne of phosphate (P_2O_5) produced, and 4.5 to 5.2 t of gypsum per tonne P_2O_5 produced are generated that require appropriate disposal. The strength of this phosphoric acid is 30 to 32% P_2O_5.

Product slurry from the reactor is introduced into the filter section and a vacuum is applied. After a dewatering period, the filter cake undergoes two or three washing stages with progressively weaker solutions of phosphoric acid. The wash-water flow is countercurrent to the rotation of the filter cake, with recycled gypsum pond water being used for the last wash; the filtrate from this step is used as the wash liquor for the preceding stage, etc. The wash from the first stage is recycled to the attack reactor.

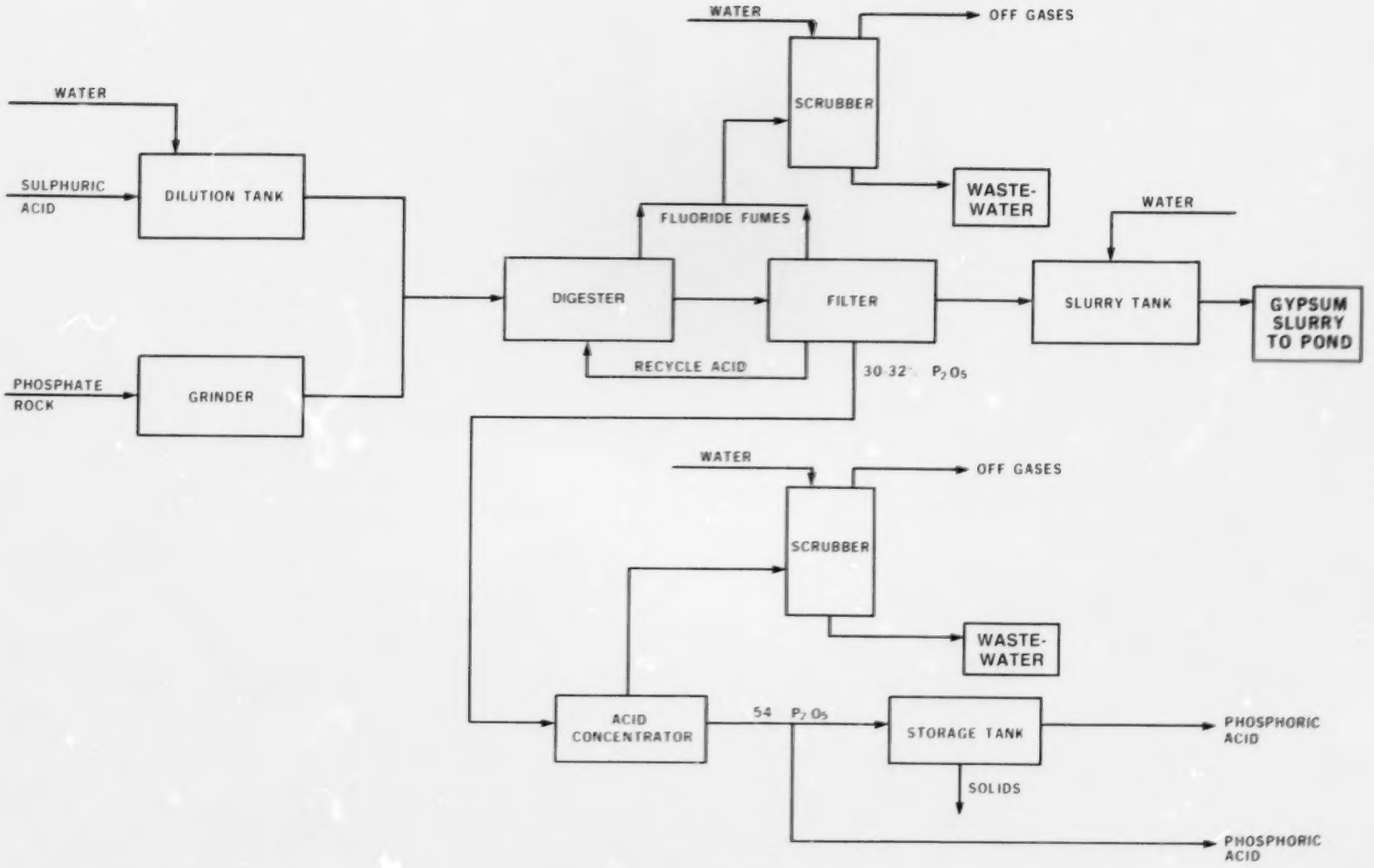


FIGURE 8 PROCESS FLOW SHEET - WET PROCESS PHOSPHORIC ACID PRODUCTION

A typical washed cake contains 18 to 35% water, with residual quantities of P_2O_5 and 0.6% fluoride (as F). The 32% P_2O_5 acid obtained from the filter generally is concentrated to 54% in a two- or three-stage vacuum evaporator system. At one plant visited, the 30 to 32% phosphoric acid goes to a thickener where any solids not removed by the filter, or any solids formed when the acid is being concentrated to around 40%, settle out. These solids are returned to the attack reactor.

Phosphoric acid free of solids, from the thickener, is sent to a Swenson evaporator where steam is supplied to concentrate the acid. The concentrated liquor flows out of the bottom of the evaporator and part of it is recycled to the thickener. Another part of the concentrated liquor is sent to an Ozark evaporator for further concentration. The vapour leaving the top of the Swenson evaporator passes through a steam separator containing baffles for further separation of the entrained liquor from the vapours. The vapour then condenses in the recycled gypsum pond water that is recycled to the barometric condenser, which is used to collapse the hot vapours, thus creating a high vacuum in the system.

The approximately 40% acid from the Swenson evaporator goes to an Ozark submerged combustion evaporator, which concentrates the acid to 54%. Because the vapour is mixed with large quantities of noncondensable gases, high entrainment losses frequently occur. The vapours and noncondensable gases at this plant first pass through a venturi scrubber, which uses fresh water, to recover P_2O_5 values. This effluent (approximately 45 L/m) is sent to the attack reactor. The fumes then pass on to a dehumidifier and three cyclonic spray scrubbers in series. Recycled gypsum pond water is used in the cyclonic scrubbers.

3.2.3 Normal Superphosphate. Superphosphate is manufactured by the acidulation of phosphate rock with sulphuric acid to form monocalcium phosphate and calcium sulphate, as shown in the following equation:

$$Ca_3(PO_4)_2 + H_2SO_4 + H_2O \rightarrow 2CaSO_4 + CaH_4(PO_4)_2 \cdot H_2O$$

The calcium phosphate is water soluble, so it can be used as a fertilizer. The product contains 30% monocalcium phosphate, 10% dicalcium phosphate, and 45% gypsum, with the remainder being impurities. Fluoride in the rock also reacts with the sulphuric acid to form hydrofluoric acid (HF). This is then converted to silicon tetrafluoride (SiF_4) and hydrolyzes to fluosilicic acid.

Phosphate rock, after grinding, is sent to a mixer to form a slurry with 65 to 75% sulphuric acid (Figure 9). This slurry is then discharged to a pug mill where

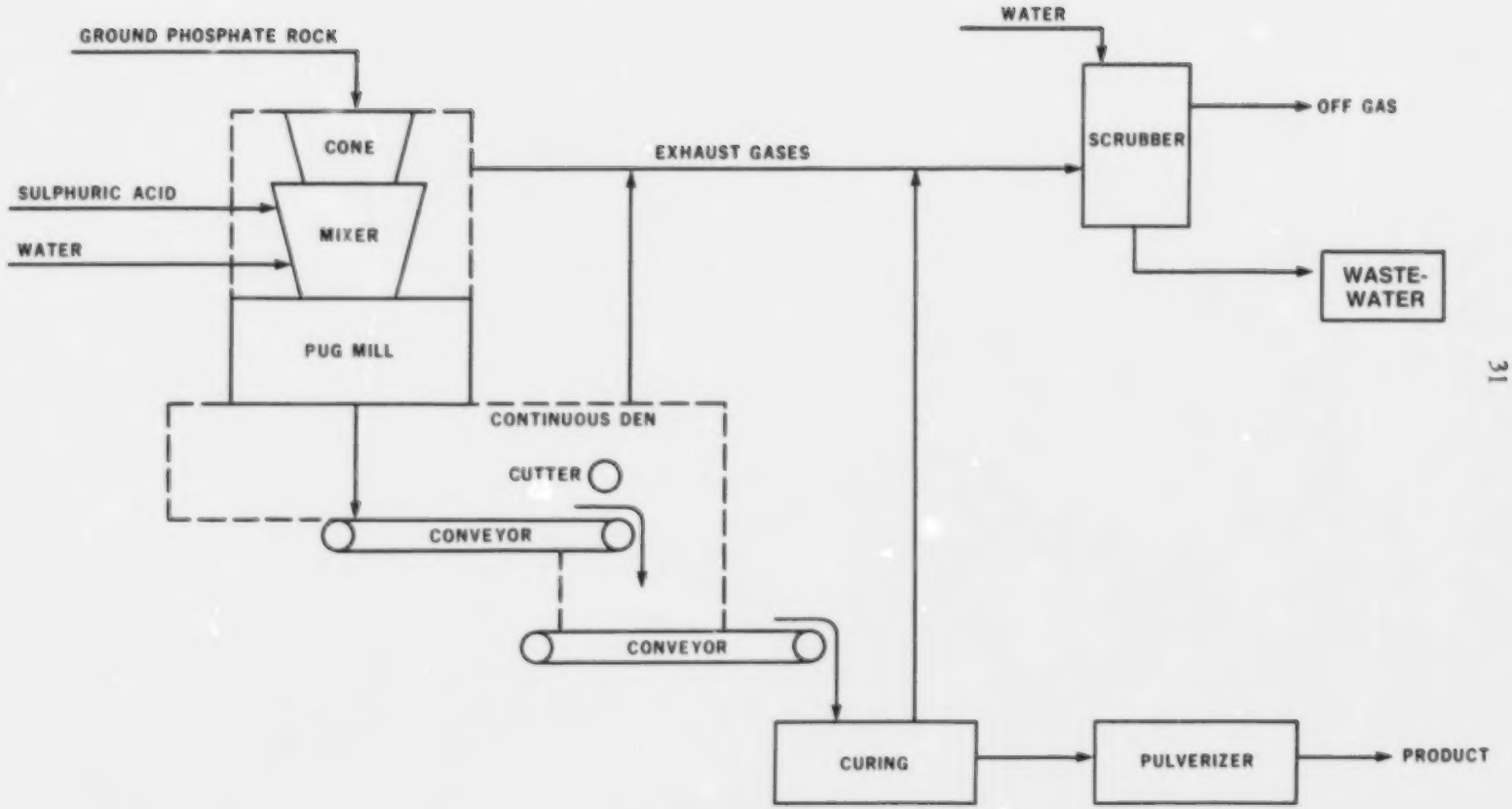


FIGURE 9 PROCESS FLOW SHEET - NORMAL SUPERPHOSPHATE PRODUCTION

additional mixing and a reaction take place. The reaction is very rapid and exothermic. Residence time in the pug mill is 2 minutes or less.

From the pug mill, the slurry discharges to a slow moving conveyor (continuous den) where the reaction continues and the slurry stiffens to form a plastic mass. Den residence time is around 20 minutes. As the plastic mass leaves the den, it is cut into chunks. The evolving gases have given it a honeycomb appearance.

The cut-up product is transferred to storage for completion of the reaction or curing. Curing takes about 2 to 8 weeks, depending upon the process. The final product is either shipped as run-of-the-pile or is granulated and stored in granular form before shipping.

If granular superphosphate is to be made, crushed or ground run-of-the-pile normal superphosphate is treated with pond water and steam or with 40% phosphoric acid in a rotating chamber. The granules pass to a dryer, followed by a screening process. The fines are returned to the granulator; the oversize is crushed in mills before being recycled to the granulator.

3.2.4 Triple Superphosphate. Triple superphosphate is becoming less important as a major fertilizer. It has been replaced by ammonium phosphate. The production process for triple superphosphate is similar to that for normal superphosphate, the only difference being that phosphoric acid is used for acidulation (Figure 10). The reaction can be written as

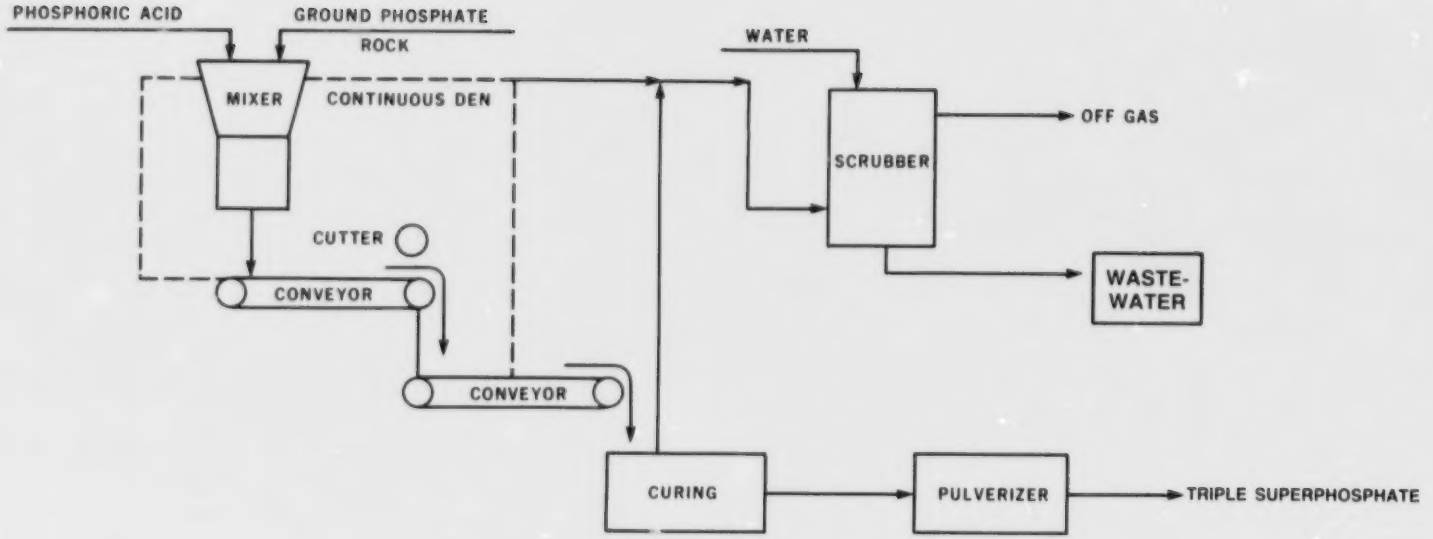
$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \rightarrow 10CaH_4(PO_4)_2{\cdot}H_2O + 2HF$$

The product contains from 44 to 47% available P_2O_5.

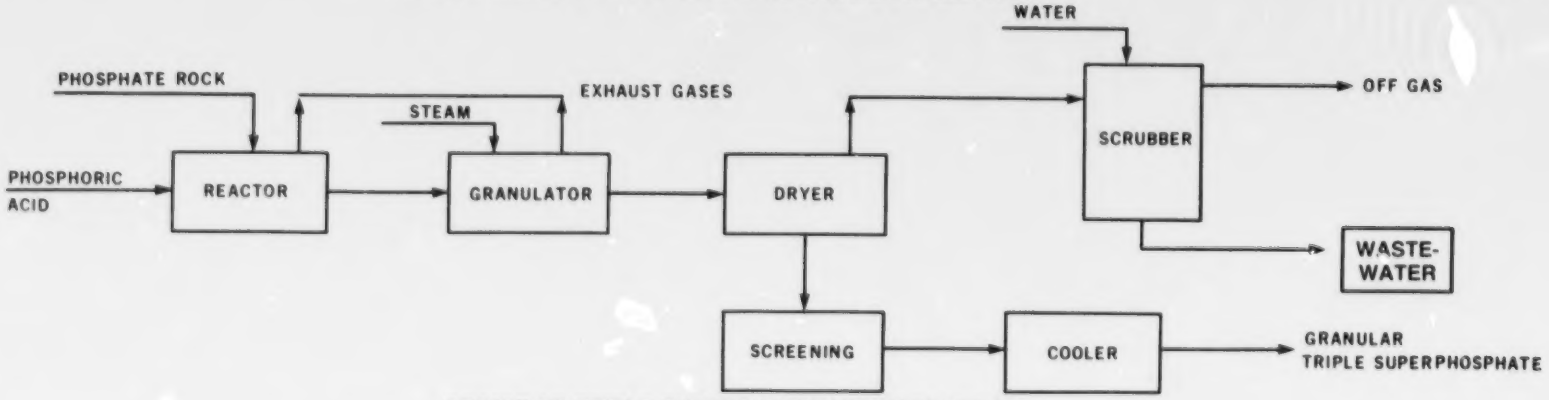
Phosphoric acid containing 52 to 54% P_2O_5 is mixed with ground phosphate rock, usually in a Tennessee Valley Authority (TVA) cone mixer or, as in the case of the plant visited (which has subsequently temporarily closed), the same equipment as noted above for normal superphosphate.

Granular triple superphosphate is made from cured run-of-the-pile triple superphosphate by treating it with water and steam in a rotary drum, followed by drying and screening.

3.2.5 Ammonium Phosphate. Ammonium phosphate fertilizers include a variety of formulations that differ in the amounts of nitrogen and phosphorus present. In a typical ammonium phosphate process, 30 to 40% P_2O_5 phosphoric acid is partially reacted with ammonia in a preneutralizer. The resultant slurry is sprayed onto a bed of fine recycled



RUN-OF-THE-PILE TRIPLE SUPERPHOSPHATE PRODUCTION



GRANULAR TRIPLE SUPERPHOSPHATE PRODUCTION

FIGURE 10 PROCESS FLOW SHEET - TRIPLE SUPERPHOSPHATE PRODUCTION

solids in a granulator. Additional ammonia is injected under the granule bed to complete the reaction. The resulting granules, which have grown in size, are dried and screened, with the undersize being recycled to the granulator and the oversize being crushed and recycled (Figure 11).

Basic reactions are

$H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$ (monoammonium phosphate)

$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2HPO_4$ (diammonium phosphate)

A variation utilizing sulphuric acid gives the following reaction, which occurs concurrently with the monoammonium phosphate reaction:

$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$ (ammonium sulphate)

The resulting monoammonium phosphate - ammonium sulphate combination could contain some diammonium phosphate. Variations include the use of HNO_3 instead of H_2SO_4, which produces nitric phosphate or ammonium phosphate nitrate.

One of the most significant process developments for ammoniated granular fertilizers is the TVA pipe-cross reactor. The reactor consists of a reaction tube (various sizes are used depending upon the desired output) to which sulphuric and phosphoric acids are added through two cross pipes. A mixture of about four parts anhydrous ammonia to one part water is added through a third pipe. The hot melt discharges from the tube into a TVA-type rotary ammoniator-granulator. Steam pressure generated in the pipe-cross reactor (PCR) provides good distribution.

Some of the advantages of the PCR over a conventional preneutralizer are

1) large amounts of phosphoric and sulphuric acid can be used in the formulations,
2) the dryer acts as a cooler, and no heat is required for drying most grades,
3) the particulate, fluorine, and chlorine losses from the process are extremely low, and
4) the reactor provides a convenient means of producing a granular monoammonium phosphate.

3.2.6 Sulphuric Acid. In Canada, virtually all sulphuric acid is produced by the contact process, using the single or double absorption process (Figure 12). All contact sulphuric acid manufacturing processes incorporate burning of sulphur or sulphur-bearing feedstocks to form SO_2, catalytic oxidation of SO_2 to SO_3, and absorption of SO_3 in a strong acid stream. The least complicated systems burn elemental sulphur. When spent

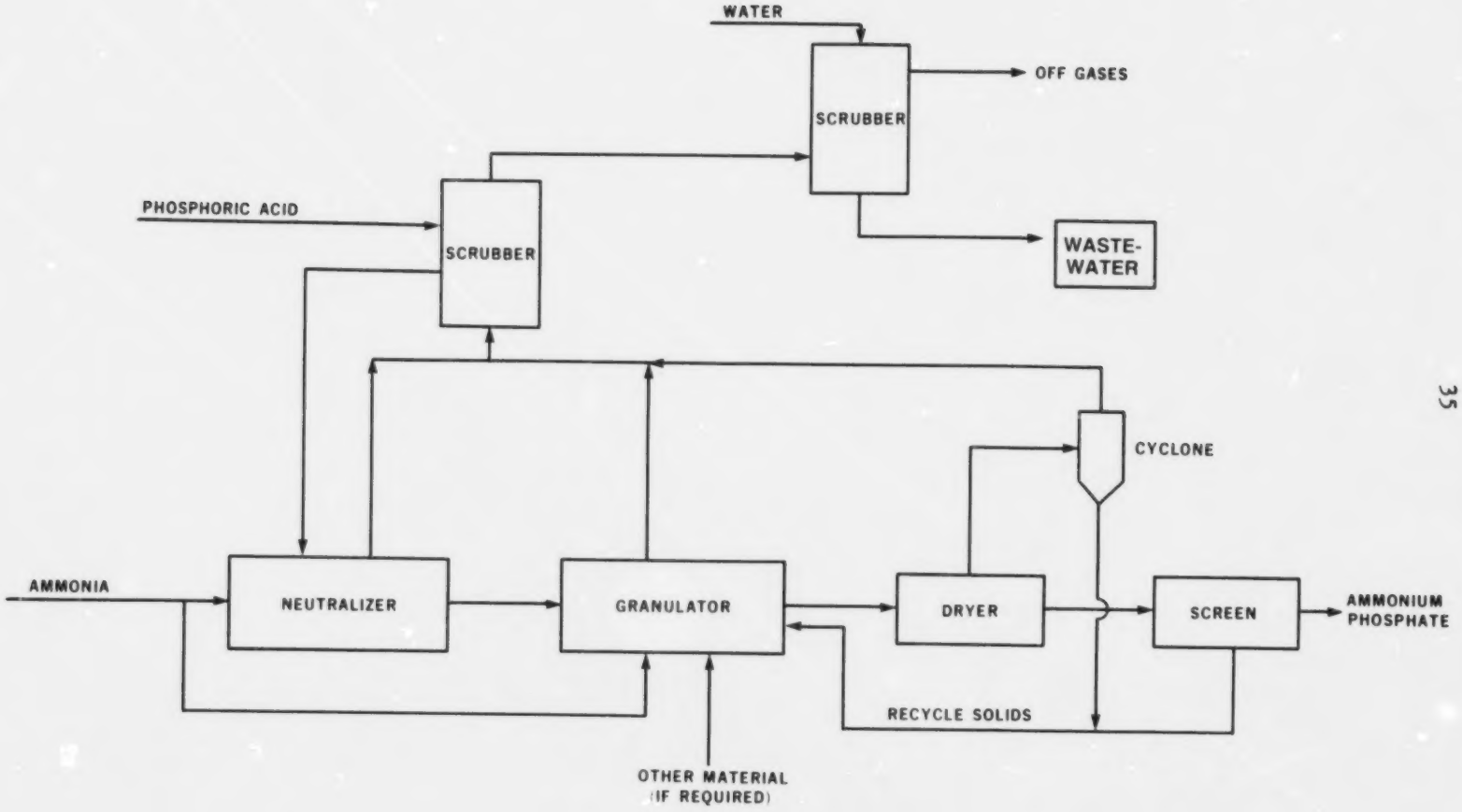


FIGURE 11 PROCESS FLOW SHEET - AMMONIUM PHOSPHATE PRODUCTION

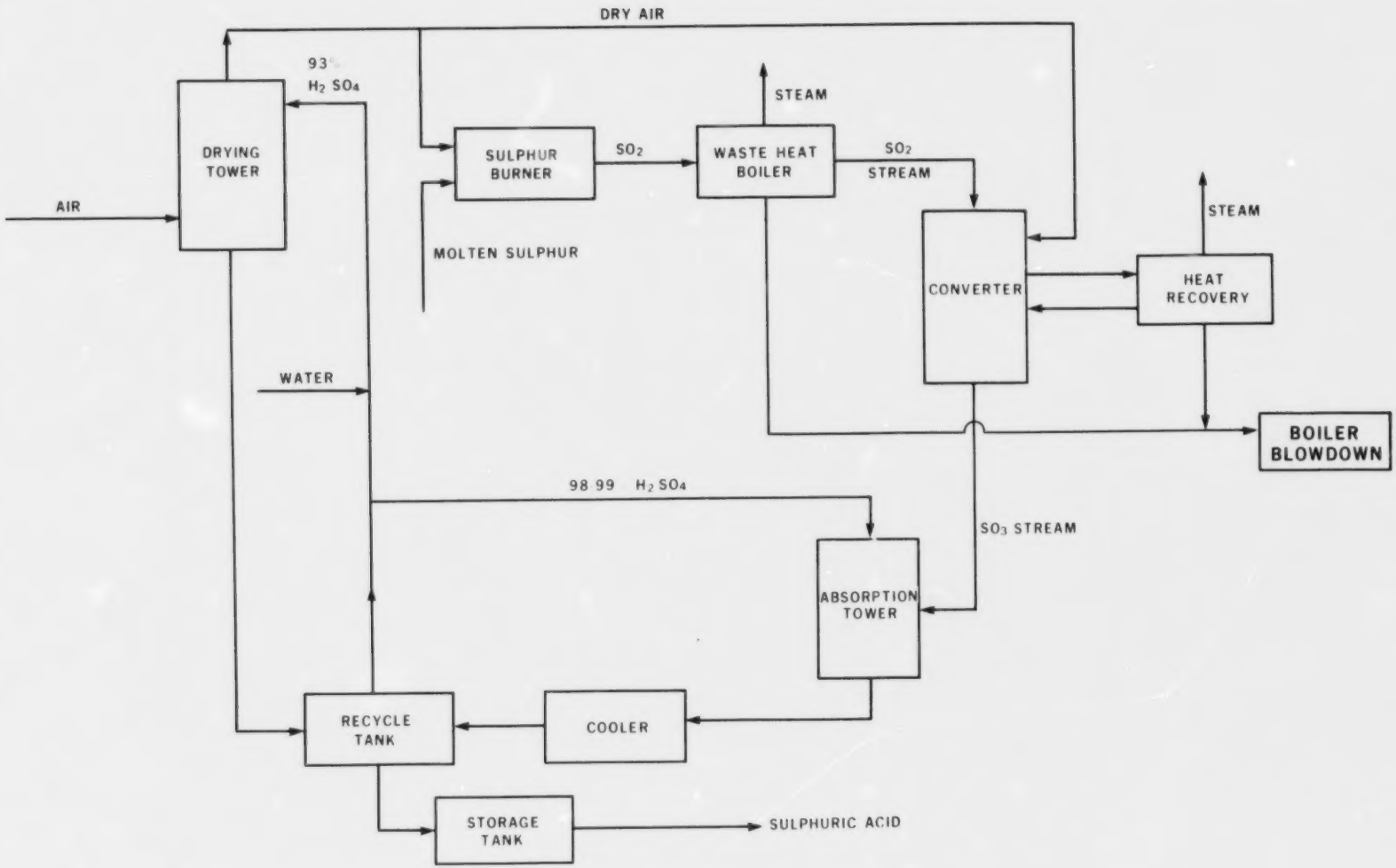


FIGURE 12 PROCESS FLOW SHEET - SULPHURIC ACID PRODUCTION

acid, sludge, and similar feedstocks are used, additional operations are required to remove moisture, organics, and particulates prior to catalysis and absorption.

When elemental sulphur is used, the molten sulphur is filtered and sprayed into a furnace to which dry air is added. This combustion air has been predried by passing it through a drying tower containing 93% sulphuric acid. The high temperature ignites the sulphur and oxidizes it to form SO_2, releasing large amounts of heat. The mixture of SO_2 and excess air is cooled by passing it through a boiler, where steam is generated and the temperature of the gaseous mixture is reduced to an optimum temperature for chemical conversion of the SO_2 to SO_3.

The cooled gaseous mixture enters the solid catalyst converter where it is converted to SO_3 in a series of steps using vanadium pentoxide or some other available catalyst. Each of the conversion steps takes place under different reaction conditions to achieve optimum conversion of SO_2 to SO_3. The gas exiting the converter is cooled in an economizer to a temperature ranging from 230 to 260°C.

Following conversion, the SO_3 gas is circulated upward through a packed absorption tower. The tower normally contains ceramic packing with 98% sulphuric acid circulating counter to the gas stream. The SO_3 is readily hydrolized to H_2SO_4 by the water in the acid. The acid strength and temperature are carefully regulated to prevent excessive SO_3 releases. The 98% acid is recycled through the absorption tower by way of the pump tank. A portion is also diluted to 93% and circulated through the drying tower. Product acid is the excess over drying tower and absorption tower recycle requirements.

In the double absorption system, which has become the choice of many sulphuric acid manufacturers, as a means of reducing SO_2 emissions from the absorption tower, a second absorption tower has been added. The second tower is installed between the first and final SO_2 to SO_3 catalytic conversion steps. This second absorption process permits the achievement of a greater conversion of SO_2 to SO_3 and significantly reduces the quantity of SO_2 in the discharged gas stream. Double absorption plants achieve SO_2 conversion efficiencies of 99.5% and better, compared with approximately 98% efficiencies for single absorption plants.

In both the single and double absorption options, cooling towers and boilers for waste heat recovery are usually standard items. Evaporation from the cooling tower acts to concentrate the water impurities, as well as the treatment chemicals used, to inhibit scale growth, corrosion, and bacterial growth. These cooling systems require a blowdown to keep impurities at an acceptable level. The only cooling water contamination from

process liquids is through leaks in the heat exchanger equipment. Contamination does occur periodically and continuous monitoring, therefore, is used to detect such failures.

4 WASTEWATER SOURCES AND CHARACTERISTICS

4.1 Nitrogen Fertilizer Industry

4.1.1 Water Use. The availability of fresh water for cooling, boiler feed, and other uses is an important consideration in choosing a plant site. Freshwater intake ranges from 3000 m^3/d, in the case of one of the smaller plants with closed-cycle cooling, to over 300 000 m^3/d in one of the largest plants with once-through cooling systems. Water treatment varies from treatment of all fresh water to only that portion required for boiler feed and potable water.

All plants in the nitrogen fertilizer industry require water that, after suitable treatment, is used for the following purposes: (1) cooling, (2) steam generation, (3) injection into the process, and (4) air pollution control devices. By far the largest amount of water is used for process cooling requirements of the plants. Cooling towers are the most commonly used method for this purpose. Warm water returning from the process plant is cooled for return circulation by intimate contact with air that is drawn through the tower by fans exhausting to the atmosphere. In the tower, cooling is achieved partially by exchange of sensible heat to the atmosphere and partially by evaporation of a portion of the water being circulated. Coincident with this evaporation is a buildup of solids in the cooling water being circulated. To prevent these solids from becoming excessive and causing fouling in the process plant heat exchangers, it is necessary to maintain a cooling tower "blowdown." To maintain a constant volume in the system, "make-up" water is added to the cooling tower at a rate equal to evaporation, "drift loss," and "blowdown" loss.

The second largest water demand in nitrogen fertilizer industry plants is for steam generation. All plants in the industry consume steam, and ammonia and nitric acid plants generate steam from waste heat boilers. In the ammonia process, 1 t of steam is normally generated for each tonne of ammonia produced. Steam is used to supply various process heat requirements, such as regeneration of absorbents and product drying, and as a source of power to drive compressors, pumps, blowers, and fans. In ammonia plants, steam is also one of the process reactants.

The quality of boiler feed water and, therefore, the method of treatment are dependent on the pressure at which steam is to be generated. The newer ammonia plants, which use centrifugal compressors, use steam at a gauge pressure of 4100 kPa and higher. Older ammonia plants and other plants in the nitrogen fertilizer industry use steam at lower pressures.

The smallest water demand is for direct use in the plants and in air pollution control devices. Water is required for direct injection into various plant processes. Steam condensate is normally used for this purpose because water containing any significant amount of dissolved or suspended solids will plug the equipment, and possibly corrode and poison catalysts in cases where they are used. In ammonia plants, water is used to make up the original charge of absorbing solutions in the gas purification section. Also, some plants use a small quantity of water for steam desuperheating. In both cases, the operating make-up requirements are supplied from recovered condensate.

In nitric acid plants, water is injected directly into the process at the top of the absorber. The quantity required is about 345 L/t of acid produced (100% basis). This is a net consumption as the water is part of the product acid produced.

Water requirements for the production of various nitrogen fertilizers are

Ammonia	230 000 - 780 000 L/t NH_3
Ammonium Nitrate	12 000 - 145 000 L/t NH_4NO_3
Ammonium Sulphate	400 - 40 000 L/t $(NH_4)_2SO_4$
Urea	80 000 - 370 000 L/t urea

4.1.2 Wastewater Sources. The main sources of pollution from the nitrogen fertilizer industry are process wastewaters originating primarily from condensation of vapour exhaust streams, which would otherwise be exhausted to the atmosphere; cooling tower, boiler, and compressor blowdown; regeneration of solutions from ion exchange systems normally used to provide feed water; wastewaters from wet scrubber air pollution control devices; sanitary wastewaters; and nonpoint sources, such as accidental spills, valve and pump-seal leaks, overflows, plant washdowns, and storm runoff.

One other possible source of pollution in nitrogen fertilizer plants is contamination of the cooling tower water by ammonia vapours that escape to the atmosphere through leaks and stack vents. This is common to most ammonia plants regardless of feedstock and process type. Water, which has a high affinity for ammonia, will absorb from the atmosphere any escaped gas if contact is made with the cooling tower. Even though the air pollution may have been of short duration, the resulting water pollution may linger for a relatively long time due to contamination of the large quantity of water contained in the cooling water system.

Most of the wastewater sources mentioned above, e.g., boiler and compressor blowdown, wastewaters from wet scrubbers, etc., are common to most of the sub-

categories within the nitrogen fertilizer industry. Process wastewaters from the different types of plants are outlined below.

Ammonia plants. In the catalytic steam reforming of natural gas process, shift gases pass to the low temperature shift converter and are cooled to approximately 55°C. Unreacted steam is condensed and separated from the gas in a knockout drum. This condensed steam is the source of more than 90% of the process wastewater. Additional condensate is removed from the cooled gas that leaves the methanator.

If the hot potassium carbonate system is used to remove carbon dioxide from the syn gas, the rich carbonate solution will flash as it enters the regenerator, producing carbon dioxide and water vapour. This vapour is condensed and is mainly returned to the regenerator; however, some wastewater might go to the sewer.

In the partial oxidation process to produce ammonia, a blowdown to remove carbon particles from the hydrogen generator and a blowdown from the water scrubber, which is used to lower the temperature of the gas after the low temperature carbon monoxide converter, are discharged to the sewer. In addition, the caustic scrubbing solution, when it is nearly utilized, is neutralized with acid and then discharged to the sewer. This caustic scrubber is used to remove carbon dioxide from the air entering the air separator and to remove carbon dioxide from the gas stream before the hydrogen gas is subjected to a low temperature.

In both processes, the CO_2 absorbing section is more susceptible to the possibility of water pollution from mishaps, such as leaks, spills, accidents, and negligence. No statistics are available as to the frequency and magnitude of pollution from such events but these are known to occur and must be recognized and considered.

Ammonium nitrate plants. The nitric acid - ammonia reaction is highly exothermic, causing large amounts of water to be flashed off and taking with it ammonia, nitric acid, nitrates, and some nitrogen dioxide. This contaminated condensate plus condensate from the vapour streams off the evaporators and solutions from wet scrubber air pollution control equipment makes up the bulk of the process wastewater.

Urea plants. Sources of process wastewater in the production of urea are the filtrate from the concentration of urea solution when crystallizers are used and the evaporator exhaust. In addition, any total recycle system requires small quantities of ammonia and carbon dioxide to be occasionally purged via wet scrubbing equipment.

Ammonium sulphate. In the production of ammonium sulphate, several gas streams are produced in the crystallizer and dryer areas. To control ammonia and particulate emissions, the gas stream from the crystallizer is either scrubbed or passes through a condenser. The dryer off gases normally are directed to a wet scrubber. These wastewaters are recycled or discharged to the sewer.

Nitric acid plants. No process wastewater effluents are normally generated by nitric acid plants. Occasional contamination can occur, however, in the cooling water cycle due to heat exchanger leaks.

Process spills and wash waters. In all process plants, inevitably there are operative spillages and leakages that result in small but highly contaminated wastewater streams. The quality of the resultant wastes is independent of plant size but could be dependent on both operating and housekeeping procedures. It is, therefore, very difficult to estimate or ascertain the volume or composition of this particular waste and no meaningful data are available.

In the majority of the plants, these effluents are collected in an underground sump for either recycling purposes or mixing with other process wastewaters to be treated prior to discharge.

Wash waters are generated from periodic equipment washing that results in large volume, low contaminant streams. Treatment of these wastes is similar to that for operational spillages.

Nonpoint source discharges. Nonpoint source discharges are generated under rainy or snow-melting conditions and can contain significant quantities of contaminants. These materials could either be absorbed airborne ammonia, urea, or ammonium nitrate dust or washed out fertilizer spills from plant shipping areas. No definitive estimate, however, of the discharge volume(s) or composition can be made.

4.1.3 Wastewater Characteristics. The nitrogen fertilizer industry is quite complex due to the various types and grades of fertilizers manufactured. Process variations, water recycling practices, and in-plant modifications can all contribute to the characteristics of effluents and their volume.

The principal contaminants encountered in nitrogen fertilizer plants are ammonia nitrogen, nitrate nitrogen, organic nitrogen, and suspended solids. Chromates and phosphates, used respectively in corrosion control and boiler feed water treatment, show up in cooling tower and boiler blowdown effluents respectively. Ammonia is found in

process condensates and is likely to be found in storm waters as a result of absorption during periods of precipitation. Nitrate nitrogen, largely from condensate from the ammonium nitrate neutralizer, is also contributed, to a much lesser extent, by spills from nitric acid manufacturing units. The source of most organic nitrogen is the urea plant. The manufacturing processes, however, provide for recycling of unreacted ammonia or other gases or recovery of ammonia for use in other processes, such as ammonium nitrate.

Wastewater characteristics from nitrogen fertilizer plants, as reported in 1984/85, are shown in Table 4. This effluent is the combined effluent from the fertilizer complex.

Cooling tower blowdown. Cooling water constitutes a major portion of the water utilized by the nitrogen fertilizer industry, so it may be uneconomical to use only a once-through system. Normally after process cooling usage, the water is cooled by natural evaporation in either noncontact cooling towers or ponds and then recycled back for process cooling. Make-up water is added to replace the evaporative and drift losses incurred in this loop, but eventually tower blowdown of this system is essential to remove the gradual buildup of dissolved solids in the recirculating water.

The tower blowdown is relatively low in contaminants and is, therefore, usually kept separate from other process waste streams. The volume and quality of the blowdown will depend on the plant circulation loop and, to a certain extent, the quality of the make-up water. Contaminants in blowdown can occur as a result of process equipment leakage; a buildup of dissolved solids in the make-up water; a buildup of the chemicals added to control scaling, corrosion, and biological growth; and absorption of ammonia and other gaseous pollutants.

Several organic and inorganic chemicals are added to the cooling water, such as chromates, zinc and phosphates for corrosion control, and some organic compounds that act as slimicides. The air in the vicinity of the cooling tower is contaminated with ammonia and other gaseous pollutants that tend to be reabsorbed back into the recirculating cooling water. Cooling tower blowdown is generated from all the process operations of nitrogen fertilizer plants, with the exception of ammonium sulphate plants.

Table 5 (3,4) indicates possible ranges in concentration of typical contaminants contained in cooling tower blowdown. This composition profile is for a composite waste stream and could vary for each plant situation. Thus, in a fertilizer complex having no urea plant, urea contaminants will be absent.

TABLE 4 NITROGEN FERTILIZER PLANTS FINAL EFFLUENT CHARACTERISTICS

Plant	Average Flow (m^3/d)	pH	Suspended Solids (mg/L)	NH_3-N (mg/L)	Organic Nitrogen (mg/L)	Nitrate Nitrogen (mg/L)	Phosphate (mg/L)	Sulphate (mg/L)	Other (mg/L)	Discharged to
CIL	303 000	7.6	-	0.80	0.07	0.47	0.01	-	-	St. Clair River
Cyanamid of Canada	23 290	8.5	11.6	61	40	34	1.0	25	0.2 (Cr)	Welland River
Nitrochem	1 700	8.8	-	700	-	480	<1 as P	-	-	St. Lawrence River
Canadian Fertilizer Ltd.*	4 118	8.4	8	1.4	-	-	0.9	912	0.6 (Zn) 1.5 (Oil & grease)	South Saskatchewan River
Cominco Ltd. Calgary	150 000	7.2	5	2	0.7	0.9	-	-	-	Bow River
Cominco Ltd. Carseland	No final effluent. Effluent goes to irrigation pond or evaporation pond.									
Cominco Ltd. Trail	85 000	2.8	6 000	25	-	-	225	1 600	2.5 (Zn) 0.01 (Hg)	Columbia River
	Contains effluent from-nitrogen and phosphate fertilizer plants.									
Esso Chemical	5 000	7.7	12	22	-	13	4	-	0.1 (Cr)	90% injection well 10% North Saskatchewan River
Sherritt Gordon**	5 700	8.5	50	130	30	25	4.5	250	0.5 (Cr) 3.0 (Ni)	North Saskatchewan River
Simplot Chemical***	1 600	6-9	24	61.5	6.9	14	10	1 990	-	Assiniboine River
Western Co-op Calgary	798	8.8	64	31	-	35	5.9	-	0.46 (Cr)	Bow River
Medicine Hat	-	7.7	-	18	1.0	42	21.9	1 890	Total dissolved solids (3 300); Fluoride (0.3)	
	No final effluent discharge. All wastewater contained and recycled or used for irrigation. The analyses shown are for seepages from the gypsum pond.									

* 1978 data. The company neglected our request for updating.

** The final effluent includes effluent from the metals refinery.

*** The total plant effluent of 1600 m^3/d flows to the river from September 15 to May 15. During the spring and summer, the plant effluent is used for irrigation.

TABLE 5 COMPOSITION OF A TYPICAL COOLING TOWER BLOWDOWN FROM A NITROGEN FERTILIZER COMPLEX

Contaminant	Concentration (mg/L)
Chromate	0-300
Phosphate	0-50
Ammonia	5-100
Nitrate	0-100
Urea	0-50
Monoethanolamine	0-10
Zinc	0-30
Sulphate	500-5000
Chloride	0-40
Oil	10-1000
Heavy Metals	0-60
Total Dissolved Solids	500-10 000
Fluoride	0-10
Biochemical Oxygen Demand	10-300
Chemical Oxygen Demand	15-400
Slimicides	0-200
Organics (miscellaneous)	0-100

Boiler blowdown. In most fertilizer plants, boiler feed water is recycled. However, the characteristics of make-up water and the addition of descaling and corrosion control chemicals necessitate periodic water blowdown to remove these contaminants from the system. Boiler blowdown waste streams can be generated at fertilizer plants manufacturing ammonia, nitric acid, urea, ammonium nitrate, and ammonium sulphate.

Table 6 (3,4) shows the typical composition of boiler blowdown from a nitrogen fertilizer complex. This stream can either be treated separately or mixed with other process water.

Compressor blowdown. In ammonia production, the wastewater stream from compressor blowdown contains high concentrations of oil and grease generated from

TABLE 6 COMPOSITION OF A TYPICAL BOILER BLOWDOWN

Contaminant	Concentration (mg/L)
Phosphate	5-50
Sulphite	0-100
Zinc	0-10
Heavy Metals	0-10
Silica	10-50
Suspended Solids	50-300
Total Dissolved Solids	500-3500
Miscellaneous Organics	0-200
Alkalinity	50-700
Hardness	50-500

synthesis gas and process air compressors. However, the exact composition of this waste stream is not known.

The combined effluent characteristics of untreated cooling water, compressor blowdown, and boiler blowdown from three plants are shown in Appendix Table D1.

Process effluent. Process effluents in nitrogen fertilizer plants usually consist of scrubber solutions and condensates. These wastes account for approximately 20 to 25% of water usage within the industry, but contain the bulk of the contaminants generated by their respective processes.

Scrubber solutions represent a sizeable and growing source of contaminated water for this industry. In the fertilizer industry, most scrubbing operations use water or aqueous solutions, which result in the formation of waste streams that must be recycled or treated prior to discharge. The concentration of pollutants in the aqueous stream can vary over wide ranges depending on gas stream concentrations and solution recycle practices, e.g., the scrubber solutions are recycled and a side stream is continuously removed to maintain the concentration in the scrubbing liquor below the equilibrium level. This side stream is normally recycled to the process.

A summary of the range in volume and composition of process effluents from various nitrogen fertilizer plants is given in Table 7 (3,5). In addition to the contaminants shown in the table, the process condensate from ammonia plants will contain methanol (1000 mg/L); methylamine, dimethylamine, and trimethylamine (all around 20 mg/L); plus small amounts of iron, copper, zinc, sodium, calcium, and aluminum.

Process effluent characteristics (scrubber solutions and condenser water), before and after treatment, are shown for three plants in Appendix Table D2.

TABLE 7 VOLUME AND COMPOSITION OF PROCESS EFFLUENTS FROM VARIOUS NITROGEN FERTILIZER PLANTS

	Ammonia	Ammonium Sulphate	Ammonium Nitrate	Urea
Volume				
Litres per metric tonne of product	400-2000	500-50 000*	200-6100	130-4000
Contaminant Concentration (mg/L)				
Ammonia	20-700	10-1000*	200-2000	200-4000
Carbon Dioxide	150-2000	-	-	100-1000
Nitrate	-	-	50-10 000	-
Sulphate	-	5-500*	-	-
Monoethanolamine	50-100	-	-	-
Urea	-	-	-	50-1000
Oil	100-10 000	-	-	10-100
Biochemical Oxygen Demand	50-150	<20	<20	50-100
Chemical Oxygen Demand	60-200	<20	<20	50-500

* wide range due to possible recycling of scrubber solutions

Process spills and wash water. In all plants, invariably there are operative spillages and leakages that result in small but highly contaminated wastewater streams. These spills can be solid or liquid depending on the particular operation. It is more or less standard practice to clean up such spills using water or acid. The spilled material is usually washed to a sump where it can be collected for recycling to the process or treated prior to discharge. In addition, wash waters are generated from periodic equipment washing, which results in large volume, low contaminant streams.

The characteristics of these effluents depend on operating and housekeeping procedures. It is, therefore, very difficult to estimate or ascertain the volume; however, the contaminants present will be the product material itself, processing intermediates, or reactants and will be similar to those shown in Table 7.

Sanitary effluent. Sanitary effluent is directed to municipal sanitary systems or septic tanks. The flow from most plants ranges from 50 to 600 m^3/d.

Raw water treatment plant effluent. Demineralization systems are widely used for conditioning water for high-pressure boilers. The ion exchange systems chosen vary according to the volumes and compositions of the raw water, the effluent quality requirements, and the comparative capital and operating costs.

When silica removal is required, the system may consist of a hydrogen cation exchanger unit and a strongly basic anion exchanger unit, usually with a degasifier between the units to remove CO_2 ahead of the strongly basic anion exchanger unit. The hydrogen cation exchanger unit removes all cations, such as calcium, magnesium, or sodium. This unit is normally regenerated using sulphuric acid, which discharges the cations to the wastewater. The anion exchanger unit will remove silicic and carbonic acids as well as sulphuric, hydrochloric, or nitric acids. This unit is regenerated with caustic soda, which discharges the Na_2SO_4 produced to the wastewater. The amounts discharged are dependent upon the quality of the raw water and the amount of steam required by the plant.

Nonpoint source discharges. It is very difficult to estimate or ascertain the volume or composition of these particular wastes and no meaningful data are available. Storm water runoff from areas within the plant boundaries used for processing and storing raw materials, finished products, and waste materials can vary in the degree of contamination depending on the plant's housekeeping practices and the volume and frequency of rainfall. Contaminants could be absorbed airborne ammonia, urea, ammonium nitrate dust, or wash-out fertilizer spills.

4.2 Phosphate Fertilizer Industry

4.2.1 Water Use. The availability of fresh water for cooling, boiler feed, and other uses has some bearing on the choice of the plant site. Freshwater intake ranges from 5400 m^3/d, with closed-cycle cooling, to over 34 000 m^3/d with a sulphuric acid plant as part of the complex and a once-through cooling system. Raw water treatment varies from treatment of all fresh water to only that portion required for boiler feed and potable water.

Most plants in the phosphate fertilizer industry require water for cooling, utilization within a process, steam generation, and air pollution control devices. By far the largest amount of water is used for process cooling. Cooling towers are the most commonly used method for this purpose. To maintain a constant volume, make-up water is added to the cooling tower at a rate equal to evaporation, drift loss, and blowdown loss.

In the production of sulphuric acid, large volumes of cooling water are required plus water is injected into the process.

In the crushing and grinding of phosphate rock process, small amounts of water are utilized for indirect cooling of lubricating oil and mechanical equipment. If wet grinding is used, some water must be added; however, this water is incorporated into the process reactants.

In the production of normal superphosphate, water is required to dilute the 98% sulphuric acid to 65 to 75%. Air pollution control devices also require water to remove fluorides, acid mist, and dust particles.

In the production of wet process phosphoric acid, cooling water, vacuum coolers, and dilution and cooling of the acid are techniques used to control process temperature. All reaction systems include a system to pass evolved gases through wet scrubbers to remove fluorides, acid mists, and particulates. The approximately 26% phosphoric acid must be concentrated, normally, to around 54% using heat exchangers and flash chambers in combination with barometric condensers. Large amounts of water are used in the barometric condensers. Recycled water is used to cool the 54% acid to optimum temperatures for storage and the precipitation of impurities.

Water requirements for the production of various phosphate fertilizers are

Phosphoric Acid	100 000 - 200 000 L/t P_2O_5
Normal Superphosphate	0 - 12 000 L/t product
Triple Superphosphate	0 - 20 000 L/t product
Ammonium Phosphate	0 - 62 000 L/t product

4.2.2 **Wastewater Sources.** Two basic wastewater source types exist in a phosphate fertilizer plant: point and nonpoint. Point sources are those that originate as a definite wastewater stream from a particular process and can be divided into three classes: contact process water, noncontact cooling water, and steam condensate. Contact process wastewater refers to any water that, during manufacturing or processing, comes into direct contact with, or results from, production or use of any material, intermediate product, finished product, by-product, or waste product. Nonpoint sources originate from leaks or runoff from developed areas within a plant.

Because of the integrated nature of the phosphate fertilizer industry, considering the wastewater handling practices of the industry as a whole is necessary. However, point sources for each of the processes are discussed separately, followed by a general discussion of nonpoint sources for the whole plant.

Phosphate rock processing. No wastewater effluents are produced by either the dry or wet grinding processes; however, around 200 m^3/d of cooling water are utilized for the indirect cooling of lubricating oil and mechanical equipment, which results in an increase in temperature only.

Normal superphosphate (NSP). The only process wastewater stream generated at NSP plants is the wet scrubber liquor used to reduce the level of fluoride gases and particulate matter evolved from the mixer, den, and conveyors. The fluoride released from the mixer and conveyor varies from 10 to 50% of the rock fluoride or 1 to 5 kg/t of product and is mainly in the form of silicon tetrafluoride (SiF_4). The emission from the conveyor areas accounts for 95% of all fluoride released.

The fluoride is scrubbed from the gas stream with water or dilute fluosilicic acid. Scrubber design, number of stages, source of water, and extent of fluoride recovery all affect the characteristics and volume of the wastewater. At most plants, the scrubber liquor is discharged to a water containment or pond system and reused.

Two plants in eastern Canada and one in western Canada manufacture hydrofluosilicic acid for the treatment of municipal water supplies, thus minimizing the release of fluorine compounds to the atmosphere and/or groundwater.

Triple superphosphate (TSP). In the manufacture of triple superphosphate, as with NSP, no wastewaters are produced except for the wash water used in area cleanup and the scrubbing liquor resulting from the control of air emissions evolved from the mixer, den, conveyors, and drying areas. The amount of fluorides released varies from 32 to 40% of the rock fluoride, with the majority being released from the mixing and conveying areas. This corresponds to 4.5 to 5.5 kg of fluoride per tonne of product. In addition to the fluorides, dust is also evolved, which must be captured and removed from the working area. Recycled gypsum pond water is normally used in the scrubber system.

Phosphoric Acid. Sources of contact process wastewater from wet process phosphoric acid (WPPA) production include wet scrubber liquor, gypsum slurry water, and barometric condensers. Disposal of the gypsum slurry is a major problem in the phosphate fertilizer industry as 1.5 t of gypsum are produced per tonne of rock processed or 4.5 to 5.0 tonnes per tonne of P_2O_5 produced.

In most cases, this slurry is sent to a holding pond to allow the gypsum to settle out. These lagoons are usually large diked areas of sufficient capacity to provide 0.22 ha/t of phosphate (P_2O_5). The gypsum usually accumulates at an annual rate

of 1356 m^3/t of P_2O_5 produced. This reservoir of contaminated process water normally supplies the water requirements for the scrubbers, for transferring waste gypsum to the disposal area, and for operating the barometric condensers.

Acid sludge underflow from the acid holding tank contains substantial amounts of phosphate and is normally sent to the attack vessel or is blended into a dry fertilizer.

Once-through or recirculated noncontact cooling water is used to control the exothermic reaction when concentrated sulphuric acid is diluted. Cooling water may be either recirculated gypsum pond water or a separate nonprocess stream that is recycled or discharged. Significant quantities of steam are used in WPPA production. Uncontaminated steam condensate can be discharged to the receiving water without treatment. Contaminated steam condensate, such as that from barometric condensers and vacuum ejectors, is discharged to the gypsum pond.

Ammonium phosphate. Substantial quantities of ammonia are volatilized from the acid neutralizer, dryer, and granulator at ammonium phosphate plants. This ammonia is recovered using weak phosphoric acid as the scrubbing liquor. The phosphoric acid scrubbing solution is recycled to the ammoniator-granulator; thus, there is no effluent. However, the phosphoric acid scrubbing solution contains some fluorides that are stripped and are removed in the secondary scrubbing system. This secondary scrubbing system, which uses water as the scrubbing liquor, removes fluorides, particulates, ammonia, and combustion products from the neutralizer, granulator, dryer, cooler, and screening operation and is, therefore, a wastewater source. In the majority of Canadian ammonium phosphate plants, gypsum pond water is used for secondary scrubbing and is, thus, contained in a water recycling system.

Sulphuric acid. The production of sulphuric acid usually does not generate any process wastewaters. Large volumes of cooling water are required by this industry. If once-through cooling water is used, there should be no contamination of the cooling water unless leaks in the cooling tubes develop. Instrumentation will detect leaks readily and corrective action can be taken immediately. If cooling towers are used, then cooling water blowdown will be required.

Steam is produced when the mixture of SO_2 and excess air, leaving the furnace, passes through the waste heat boiler to reduce the gaseous mixture to an optimum temperature for chemical conversion of SO_2 to SO_3. Steam is also produced when the SO_3 gas leaving the converter passes through the economizer. This steam is

used throughout the plant; however, to maintain the maximum level of dissolved and suspended solids in the system, a blowdown is required.

4.2.3 Wastewater Characteristics. If untreated process wastewaters from phosphate fertilizer manufacturing were discharged regularly, long-lasting or permanent environmental damage to surface water ecosystems could result. Treatment practices would be very expensive; thus, gypsum ponds and cooling ponds with essentially complete recycle are used. Normally, the only wastewaters discharged from these plants are some runoff, cooling tower blowdown, and some wash waters. Wastewater characteristics from phosphate fertilizer plants are shown in Table 8.

Phosphoric acid. The gypsum pond is an integral part of the wastewater treatment scheme at a typical phosphate fertilizer complex. The pond serves as a settling basin for gypsum and other solid wastes and functions as a reservoir for recycling process water and cooling water.

Clarified pond water can be recycled and used for diluting sulphuric acid, in scrubbers and barometric condensers, and for slurrying waste gypsum from the filtration process. With each recycle, the level of dissolved contaminants in the water increases, which results in the impurities approaching equilibrium concentrations. A typical analysis of gypsum pond water is shown in Table 9. In addition to the concentrations listed in the table, gypsum pond water also contains small amounts of cadmium, chromium, zinc, vanadium, arsenic, uranium and radium 226. Usage rates for contaminated water are estimated to be 15 000 to 21 000 L/t of acid produced.

Uranium 238 and ^{226}Ra are essentially in radioactive equilibrium in the ore and after beneficiation contain around 3.7 Bq/g for Florida phosphate rock and around 2.59 Bq/g for Western phosphate rock. In the production of phosphoric acid, the radioactive equilibrium is disrupted, with uranium going mainly in the acid and radium favouring the phosphogypsum. Radium 226 is a decay product of uranium that occurs in the recycled gypsum pond water in the 1.48 to 2.59 Bq/L range. Dried areas of ponds are a possible source of radioactive emissions to the air.

Normal and triple superphosphates. When NSP and/or TSP plants are operated in conjunction with a wet process acid plant, recycled gypsum pond water is used; thus, it is impossible to characterize wastewaters from NSP or TSP plants. If a gypsum pond is not available, the effluent is sometimes retained in a pond where the fluosilicic acid concentration can build up to economically recoverable levels.

TABLE 8 CHARACTERISTICS OF WASTEWATER FROM PHOSPHATE FERTILIZER PLANTS

	pH	Suspended Solids (mg/L)	Total Dissolved Solids (mg/L)	Zinc (mg/L)	Silica (mg/L)	Chromium (mg/L)	Sulphate (mg/L)	Phosphate (mg/L)	Fluoride (mg/L)	Other (mg/L)	Remarks
CIL	-	-	-	<0.1	-	Nil	<0.1	<0.1	<0.1	-	About 39 000 m^3/d is recycled to gypsum pond.
	Once-through cooling water only; discharged to St. Clair River.										
Cominco, Trail	2.8	6 000	3 500	2.5	-	-	1 600	230	100	NH_3-N (25) Hg (0.010)	Ways of reducing contaminants in discharges used.
	Effluent from phosphate fertilizer plant combined with effluent from nitrogen fertilizer plant.										
Esso Chemical	7.7	12	-	-	-	0.1	-	4	-	NH_3-N (22) NO_3-N (13)	Effluent from phosphate plant recycled to gypsum or cooling ponds.
	Wastewater from the phosphate plants combined with a small amount (10%) of effluent from the nitrogen fertilizer plant.										
Sherritt Gordon	Effluent from the phosphate fertilizer plant is completely recycled to the gypsum pond.										
Simplot Chemical	Phosphoric acid purchased. Phosphoric acid used to make phosphate solution fertilizers.										
Western Co-op, Calgary	No discharge. Gypsum pond water recycled to plant. Some seepage might go to groundwater.										
Western Co-op, Medicine Hat	This plant is temporarily closed.										
Cominco, Kimberley	7.0	10	NIA	0.5	NIA	NIA	NIA	1.1	1.1	NH_3-N(0.1)	Discharged to river.
Belledune Fertilizer	2.5-3.0	18 300	28 600	0.5-0.7	180-200	0.2	7 600	690	310	-	Discharged to the ocean.

Note: NIA, no information available

TABLE 9 TYPICAL ANALYSIS OF GYPSUM POND WATER

Plant	Phosphate (P_2O_5)	Fluoride (F)	Sulphate (SO_4)	Calcium (Ca)	NH_3-N	Silica (Si)	pH
CIL	18 000	7 500	7 000	820	1 600	2 200	2.1
Esso Chemical	9 000	7 000	-	-	-	-	1.5
Sherritt Gordon	13 400	3 810	14 250	650	5 830	-	2.2
Western Co-op							
Calgary	1 200	8 000	4 000	1 400	850	50	1.1
Medicine Hat	648	300	2 025	-	89	-	3.9
Cominco							
Kimberley	2 000	3 000	4 000	800	200	1 500	2

Note: all values, except those for pH, in mg/L

Ammonium phosphate. The primary source of process effluents in ammonium phosphate plants is from the scrubbing of gases from the neutralizer, granulator, and dryers. All these emissions contain ammonia and fluorides that are scrubbed first with weak phosphoric acid and then with gypsum pond water. The weak phosphoric acid - ammonia solution is reused in the neutralizer and the pond water is recycled to the gypsum pond. Spills and leaks go to a sump and are normally recycled to the phosphoric acid plant. Thus, there is normally no wastewater discharged from these plants.

At one plant, where the gypsum slurry is discharged directly into the ocean, seawater is used in the scrubbers. As noted below, the contaminant concentrations using once-through seawater versus recycled gypsum pond water are considerably lower.

	Pond Water	Once-Through Seawater
Phosphate (P_2O_5)	15 000	16
Sulphate (SO_4)	9 500	3 600
Fluoride (F)	6 800	300
NH_3-N	1 600	2

Cooling water blowdown. As previously indicated, cooling water is required in the production of phosphoric acid and sulphuric acid. The cooling water from the wet

process phosphoric acid and sulphuric acid plants is fairly free of contaminants; thus, after some cooling and, if need be, pH adjustment, it can be discharged to a receiving stream. If cooling towers are used, the solids content of the water will increase, establishing the need for a blowdown. The composition of a typical cooling tower blowdown is given in Table 10 (4).

TABLE 10 COMPOSITION OF A TYPICAL COOLING TOWER BLOWDOWN FROM A PHOSPHATE FERTILIZER COMPLEX

Contaminant	Concentration
Chromate	0-250
Sulphate	500-3000
Chloride	35-160
Phosphate	10-50
Zinc	0-30
Total Dissolved Solids	500-10 000
Suspended Solids	0-50
Slimicides	0-100

Note: all values in mg/L

Boiler blowdown. The composition of the boiler blowdown will be similar to that shown for nitrogen fertilizers.

Process spills and wash waters. Process spills and wash waters from the various plants go to the gypsum pond. (Process spills and leaks from ammonium phosphate plants are recycled to the phosphoric acid plant or are sent to the gypsum pond.) No data are available from the questionnaires relative to volumes or contaminant concentrations.

Nonpoint source discharges. In any plant, various nonpoint sources can contribute to wastewater volumes, e.g., dry fertilizer material will dust over the general plant area and then be dissolved by rain or melting snow. The magnitude of this source is a function of operating practices, housekeeping, rainfall, and the design of the general plant drainage facilities. Runoff and drainage are collected and treated before discharge, if necessary, or sent to the pond for containment. Noncontaminated waters are kept segregated where possible and discharged without treatment.

Drainage from gypsum piles may be a significant contributor to the overall water handling requirements of a plant.

The potential exists for chemical and radiological contamination of groundwater as a result of seepage from gypsum stacks and large process water cooling ponds. Existing data are inconclusive and insufficient to determine the possible extent of this contamination. The potential impacts as a result of seepage need to be determined on a site-specific basis. Seepage can be reduced or prevented if it is a problem by lining ponds and underlaying gypsum piles with an impervious material.

4.3 Sampling and Analytical Procedures

4.3.1 Monitoring and Recording Procedures Used by Companies. Liquid effluent from all plants is sampled on a daily basis, some by grab samples and others on a continuous basis. Testing is carried out on the composite samples either daily or, in some cases, on a weekly basis and reported to the appropriate provincial environmental authority on a monthly basis. All information available from the questionnaire is tabulated in Appendix Tables B1 to B6.

4.3.2 Analytical Methods Used by Companies. The testing methods used by different plants for measuring various parameters are compiled in Appendix Tables B7 and B8.

4.3.3 Methods Used in the Screening Survey. The presence of any of the 129 U.S. Environmental Protection Agency listed priority pollutants in final effluent from nitrogen and phosphate fertilizer plants was established by sampling five plants, which should represent the entire cross section of the fertilizer industry. All the sample locations were selected after discussions with plant personnel. The procedure used is outlined in Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations, published in the U.S. Federal Register, dated December 3, 1979. Factual information was derived from the chemical analyses and flow measurements of representative final effluents from these plants.

Metals. Twenty-four hour composite samples of final effluents were collected during screening surveys, as well as during monitoring surveys, carried out over the past few years by governmental agencies as well as by company personnel. Metal analysis is readily determined by atomic absorption spectroscopy or by using an inductively coupled argon plasma optical emission spectrophotometer. Mercury is normally determined by the automated cold vapour technique. The priority metals found in the final effluent from fertilizer plants are shown in Tables 11 and 12.

TABLE 11 SUMMARY OF PRIORITY METAL CONCENTRATIONS FOUND IN THE FINAL EFFLUENT FROM NITROGEN FERTILIZER PLANTS

Pollutant	Concentration (mg/L)		Intake Water (mg/L)
	Average	Range	
Antimony	<0.01	<0.01	<0.01
Arsenic	0.13	<0.5 x 10-5 - 0.60	<0.05
Beryllium	<0.01	<0.001 - 0.014	<0.004
Cadmium	<0.017	<0.002 - 0.07	<0.004
Chromium	1.38	0.15 - 4.6	<0.02
Copper	0.04	0.01 - 0.18	<0.03
Cyanide (Total)	<0.04	<0.005 - 0.05	<0.04
Lead	0.05	<0.01 - 0.22	<0.01
Mercury	<0.01	<0.2 x 10-6 - 0.066	<0.0002
Nickel	<0.04	<0.01 - 0.16	<0.02
Selenium	0.073	<0.005 - 0.41	<0.02
Silver	0.010	<0.002 - 0.68	0.01
Thallium	0.014	<0.01 - 0.025	<0.03
Zinc	0.23	0.10 - 0.63	0.02

Organic pollutants. Of the 32 samples collected from the fertilizer manufacturers, 26 were duplicated for quality control. Of these, six were spiked with pesticides, six with polychlorinated biphenyls (PCBs), and 14 with base neutral and acid extractables.

For analysis at the Wastewater Technology Centre laboratory in Burlington, quantitation was done by gas chromatography - mass spectrometry (GC-MS) using d-10 anthracene as the internal standard, except for the pesticide and PCBs, which were quantitated using an electron capture detector. Base metals and acids were analyzed on an SE-54 fused silica capillary column. Volatiles and pesticides of PCBs were done on packed columns.

The analysis for organochlorine pesticides and PCBs was done by gas chromatography using an electron capture detector. A known amount of standards was added to 1 L of sample to a level of 400 ng per component (nine pesticides were used). Twice as much (800 ng) was used for DDE, DDT, and endosulfan sulfate. The recovery of

TABLE 12 SUMMARY OF PRIORITY METAL CONCENTRATIONS FOUND IN THE FINAL EFFLUENT FROM PHOSPHATE FERTILIZER PLANTS

Pollutant	Final Effluent (mg/L)		Intake Water (mg/L)
	Average	Range	
Antimony	<0.1	-	<0.1
Arsenic	0.51	0.43 - 0.60	0.12
Beryllium	<0.01	-	<0.01
Cadmium	0.329	0.002 - 0.07	0.01
Chromium	1.6	0.17 - 4.4	0.03
Copper	0.02	0.01 - 0.04	<0.02
Cyanide	<0.02	<0.005 - <0.02	<0.02
Lead	0.10	0.03 - 0.21	0.025
Mercury	0.03	0.003 - 0.06	0.003
Nickel	0.04	<0.03 - 0.07	0.01
Selenium	0.38	-	0.05
Silver	<0.02	-	<0.02
Thallium	<0.1	-	<0.1
Zinc	0.20	0.10 - 0.31	0.03

this mixture from distilled water was very good: 96 $\pm$ 6% average recovery for the nine components. The $\pm$ here does not refer to several samples but rather the several components in the mixture. PCBs were measured as a whole (average of five peaks) and spiked at 1.2 µg/L. The recovery from water was 83%.

Although the average recoveries and the deviation from the means have little intrinsic value, they are useful as a comparison between samples. A large deviation from the mean shows that some compounds might not have been recovered at all, whereas others might have shown 200% recovery due to interference. The final effluents of three fertilizer plants gave an average recovery of 87 $\pm$ 20% (Belledune, Nitrochem, and Esso), whereas recoveries of 34 $\pm$ 20% were obtained for the other two plants.

For base neutral and acid extractables, a mixture of 10 compounds (three acids and seven base neutrals) was used for spiking, at 250 µg/L. The range of properties of the compounds involved is much wider and the recoveries vary tremendously from one

compound to the next. The recovery of the acids from water was 60 ± 25% and of the base neutrals 87 ± 57%. The fertilizer samples gave poor recoveries, ranging from 8 to 25% with deviation from the means ranging from 1 to 36% for the acid extractables, and ranging from 10 to 60% with deviations from 8 to 30% for the base neutrals. Although better recoveries were obtained for final effluents than for primary effluents, the differences were not statistically significant.

Purge and trap/gas chromatography techniques were used for monoethylamine determinations. Monoethylamine's miscibility in water and its volatility were two reasons the purge and trap method was chosen to obtain a spectrum of volatile components.

For other analyses, standard accepted methods were used. The levels of priority organic pollutants found in fertilizer plant final effluents are shown in Appendix Tables C3, C4, and C7.

Aquatic toxicity testing. Composite samples of the final effluent were collected for acute lethality testing from most of the plants. Toxicity testing methods are available for evaluating the effects of chemical substances on aquatic life. The two most commonly applied are acute lethality tests and chronic tests.

Acute lethality. Acute lethality tests are generally considered to provide rapid and reproducible concentration-response curves for identifying and estimating the effects of chemicals on aquatic organisms. These tests provide the most practical means for

1) evaluating the relative toxicity of a number of chemicals,
2) evaluating the upper limit of the range of concentrations producing toxic effects,
3) evaluating the relative sensitivity of different aquatic organisms to a chemical,
4) evaluating the effects of water quality on toxicity of chemicals, and
5) developing a knowledge of the nature of the concentration-response relationship and the significance of the duration of exposure on toxicity.

Chronic. The general limitation of acute lethality tests in evaluating toxicity is that the results of such tests usually do not provide information on sublethal or cumulative effects. Chronic tests, measuring the effects of chemical exposure on the reproductive process, are useful because the empirical observations represent a total effect of all important sublethal effects, e.g., assimilation, metabolism, etc., on life processes, such as growth, reproduction, respiration, etc. The results of such studies, which usually involve exposure over a complete life cycle of the test population, provide

empirical information on the effects of chronic exposure on the species in question, identify those chemicals that may be cumulatively toxic, allow one to estimate chronically safe concentrations for closely related species, and are useful in deriving water quality criteria for the protection of aquatic life.

The U.S. Environmental Protection Agency (EPA) derived water quality criteria for a large number of chemicals tested individually. Acute and chronic tests were carried out for both freshwater and saltwater aquatic life. The values pertaining to the organic chemicals found in fertilizer plant effluents are shown in Table 13.

Normally, chemical plant effluents contain a variety of classes of chemicals and a range of concentrations. A major consideration in the environmental testing of complex chemical mixtures is that such mixtures are potentially capable of causing additive, antagonistic, or synergistic responses in test organisms.

Biological testing. In addition to collecting samples for chemical analysis and aquatic toxicity testing, 23-L, 24-hour composite samples of the final effluent, from the five plants monitored, were collected and shipped to the British Columbia Cancer Research Centre in Vancouver for testing for potential genotoxic activity.

To establish with absolute certainty the degree of hazard posed by a particular material would require testing of all potential target organisms for their various responses. In light of the large number of complex mixtures entering the environment, it is readily apparent that the cost, in terms of both time and money, of making such an assessment would be staggering. On the other hand, predictions concerning potential hazards based on the response of a single species to a chemical mixture have an unacceptably low level of certainty.

One method of increasing the level of confidence is to use a battery of tests and develop an estimate of potential based on the pooled results. This group of tests would ideally attempt to represent as broad a spectrum as possible.

Several *in vitro* short-term bioassays are available to screen chemicals for mutagenic or potential carcinogenic activities. For this study, the extract from each effluent was prepared and tested for mutagenic potential by assaying for the capacity to

1) induce mutations in *Salmonella typhimurium* (salmonella mutagenicity test),
2) induce chromosome abnormalities in cultured Chinese hamster ovary (CHO) cells (chromosome aberration test),
3) inflict damage to DNA of cultured human fibroblasts (DNA repair test), and
4) inhibit repair of DNA damage in cultured human fibroblasts (DNA repair inhibition test).

TABLE 13 PRIORITY ORGANIC POLLUTANTS FOUND IN THE FINAL EFFLUENT FROM FERTILIZER PLANTS: CONCENTRATION RANGE AND AMBIENT WATER QUALITY CRITERIA PROPOSED BY EPA

Parameter	Levels Found in Fertilizer Effluent (µg/L)	Proposed EPA Criteria				
		Freshwater Aquatic Life (µg/L)		Saltwater Aquatic Life (µg/L)		Human Health (µg/L)
		Acute	Chronic	Acute	Chronic	Estimated
Dichloromethane	2-2 360	224 000	-	-	-	1.9*
Chloroform	31-189	28 900	1 240	-	-	1.9*
Bromodichloromethane	4-130	11 000	-	12 000	6 400	1.9*
1,2-Dichloropropene	0-5	-	-	-	-	87
Trans-1,2-Dichloropropene	0-9	-	-	-	-	87
Trichloroethylene	0-2	45 000	-	2 000	-	27*
Dibromochloromethane	0-2	11 000	-	12 000	6 400	1.9*
Bromoform	0-10	29 300	6 400	24 400	-	-
1,1,2,2-Tetrachloroethane	0-10	9 320	2 400	9 020	-	1.7*
Tetrachloroethylene	0-150	5 280	840	10 200	450	8.0*
Toluene	0-30	17 500	-	6 300	5 000	14.3
Acenanhthylene	0-2	-	-	-	-	-
Pyrene	0-10	-	-	-	-	-
N-nitrosodimethylamine	0-10	-	-	-	-	0.014*
Butyl Benzylphthalate	0-92	940	220	2 944	3.4	-
Di-n-butylphthalate	0-11	730	-	2 944	-	34 000
Di-n-octylphthalate	0-14	940	-	2 944	-	-
Bis (2 ethylhexyl) phthalate	0-135	940	3	2 944	-	15 000
2,4-Dinitrophenol	0-1	230	150	4 850	-	70
Pentachlorophenol	0-4	55	3.2	53	34	1 010
Phenol	0-20	10 200	2 560	5 800	-	3 500
Benzene	0-127	5 300	-	5 100	700	6.6*
Chlorobenzene	0-6	250	50	160	129	488
1,1,2,2-Tetrachloroethene	0-3	-	-	-	-	-
Trichlorofluoromethane	0-2	11 000	-	12 000	6 400	1.9*
Chloromethane	0-468	11 000	-	12 000	6 400	1.9*

Note: Source: Ambient Water Quality Criteria. U.S. Environmental Protection Agency reports.
(-) Information not available.
* The levels that may result in incremental increase of cancer risk over a lifetime are estimated to be 1 in 100 000 population.

In addition, each straight effluent sample was tested for mutagenic activity using the "salmonella" mutagenicity test.

These tests are not considered to be as suitable for the estimation of hazard as epidemiological data or long-term whole-animal studies. For this reason, short-term tests are not used to provide "definitive" evidence that a chemical is hazardous. Rather, they are considered to provide "suggestive" evidence of a chemical's potential to cause genotoxic effects in humans. A positive Ames test does not necessarily show that a compound is carcinogenic, whereas a negative result does not rule out that possibility. Overinterpretation at this stage of research, especially with respect to relative hazard, should be avoided. As a screen to aid investigators in ordering priorities, short-term *in vitro* testing appears to be a valid approach.

5 EMISSION SOURCES AND CHARACTERISTICS

5.1 Emission Sources from Nitrogen Fertilizer Plants

5.1.1 Ammonia Plants.

Catalytic steam reforming process. Air emissions from an ammonia plant using the catalytic steam reforming process result from regeneration of the desulphurization beds, combustion gases emitted from the radiant heat section of the primary reformer, regeneration of the carbon dioxide scrubbing solution, steam stripping of process condensate (if this practice is used at the plant), purge gas from the ammonia synthesis loop, and fugitive emissions.

Partial oxidation process. Air emissions from an ammonia plant using the partial oxidation process result from regeneration of the desulphurization beds, removal of impurities in the nitrogen scrubbing unit, regeneration of the carbon dioxide scrubbing solution, and fugitive emissions.

5.1.2 Ammonium Nitrate Plants. Air emissions from ammonium nitrate plants are generated in the following process steps: solution formation (from the neutralizer and evaporator/concentrators), solids formation (prill tower or granulator), and solids finishing (predryer, dryer, cooler, coater, handling, and storage). In addition, there is the potential for fugitive air emissions from vents, seals, spills, storage tanks, compressors, pumps, and relief valves.

5.1.3 Urea Plants. Air emissions from urea plants are generated in the following process steps: solution formation (from the reactor and concentrator), solids formation (prill tower or granulator), and solids finishing (cooler, coater, screens, handling, and storage). In addition, there is the potential for fugitive air emissions from vents, seals, spills, storage tanks, compressors, pumps, and relief valves.

5.1.4 Ammonium Sulphate Plants. Air emissions from ammonium sulphate plants result from the entrainment of particles in the air flowing through the dryer, from the screening operation, and from handling, storing, and bulk loading.

5.1.5 Nitric Acid Plants. Air emissions from the manufacture of nitric acid are present in the tail gas from the absorption tower, which contains unabsorbed oxides of nitrogen. The emissions are primarily nitric oxide and nitrogen dioxide, with small amounts of nitric acid mist. Faulty equipment, such as pumps and compressors, leads to lower pressures and leaks, which decrease plant efficiency and increase emissions.

5.2 Air Emission Characteristics

The major emission problems associated with the nitrogen fertilizer industry are ammonia; particulates from prill towers, granulators, dryers, screens, coolers, and elevators; and oxides of nitrogen resulting from different operating practices and from certain processes. The following sections characterize the emissions associated with each product.

5.2.1 Ammonia Plants.

Desulphurization. Natural gas contains sulphur compounds, mostly hydrogen sulphide and carbonyl sulphide, that must be reduced to as low a level as is economically possible to prevent poisoning of the nickel catalyst in the primary reformer. Most of the ammonia plants in Canada use activated carbon fortified with a metallic oxide additive for feedstock desulphurization. Each plant has a dual tank system so that one tank is always on-stream while the other is being regenerated. Regeneration of this activated carbon tank may cause emissions of sulphur dioxide, hydrogen sulphide, hydrocarbons, and carbon monoxide.

The desulphurization tank is regenerated by passing steam through the bed for approximately 12 hours. The metallic sulphide is converted to metallic oxide and elemental sulphur. However, the sulphur, to some extent, will be lost by vaporization and it will react to form H_2S and SO_2.

Sulphur emissions based on EPA data (6), corresponding to a 24-hour emission factor, are 0.019 g SO_2 per kilogram of ammonia produced and 0.010 g H_2S per kilogram ammonia. Long-chain hydrocarbons are collected in the desulphurization tanks. Emission factors during regeneration are 3.6 g hydrocarbons (HC) (measured as methane) per kilogram ammonia and 6.9 g CO per kilogram ammonia.

Alternatively, the problem of regeneration emissions can be eliminated by the substitution of zinc oxide for activated carbon desulphurization beds. The normal design life of a zinc oxide bed is 1 to 2 years depending on the sulphur content of the natural gas. The spent bed is disposed of by landfill or sale for recovery of the zinc oxide.

Primary reformer. Natural gas and sometimes purge gases are fired at 1200°C with excess air in the radiant heat section of the primary reformer. The hot combustion gases are cooled by a series of waste heat boilers before being vented to the atmosphere. Emission species from this source consist of natural gas combustion products, i.e., SO_x,

NO_x, CO, particulates, and hydrocarbons. Levels of emissions, calculated from data on the combustion of natural gas, in U.S. ammonia plants (with no purge gas added) are (6)

Oxides of Sulphur	0.0024 g/kg NH_3
Oxides of Nitrogen	0.5 g/kg NH_3
Carbon Monoxide	0.068 g/kg NH_3
Hydrocarbons	0.012 g/kg NH_3
Particulates	0.072 g/kg NH_3

If ammonia producers use purge gas for approximately 15% of the energy input into the primary reformer (radiant heat section), nitrogen oxide emissions will increase to around 2.7 g/kg of ammonia produced. If the overhead gases from a condensate steam stripper are added to the primary reformer stack gases, the NO_x emissions will increase to around 3.9 g/kg of NH_3 produced.

Regeneration of the carbon dioxide scrubbing solution. Carbon dioxide is removed from the process (or shift) gas by absorption in an amine solution, a Sulfinol solution, or a carbonate solution. As the solutions become saturated with carbon dioxide, they must be regenerated, resulting in emissions of mainly CO_2 - about 1.2 t of CO_2 per tonne of NH_3 produced - with smaller amounts of water vapour, ammonia (1.0 kg/t), carbon monoxide (1.0 kg/t), methane (<0.75 kg/t), and small amounts of the scrubbing media (6). Carbon dioxide is separated from the scrubbing solution by steam stripping, heating, or flashing.

In the Sulfinol system, the solvent consists of an alkanol amine, water, and tetrahydrothiophene dioxide. In this system, the carbon dioxide is separated from the scrubbing solution by steam stripping and by heating. The stripped gas, containing mostly CO_2 plus small amounts of water, hydrocarbons, sulphur compounds, ammonia, carbon monoxide, and amines, is used in the urea plant and/or sold to a third party, or discharged to the atmosphere.

As the amine solution removes any residual H_2S and COS and the carbon dioxide from the process gas, other compounds are also absorbed. These absorbed compounds chemically degrade the amine. In the reboiler, the recovered amine solution is pumped back to the scrubbing system. The breakdown products are removed from the reboiler and are incinerated by an authorized disposal company.

Condensate stripper. Process condensate forms upon cooling the syn gas after passing through the low temperature shift converter and in the knockout drum after the methanator. This water contains quantities of ammonia, carbon dioxide, methanol, and

trace elements. This effluent can be sent to steam strippers to remove ammonia, methanol, and carbon dioxide, which is now present in the overhead.

Fugitive emissions. Sources of fugitive ammonia emissions are storage tanks and their pressure relief valves, ammonia compressors, spills, during loading, and pumps. These leakages are held to a minimum because the threshold limit value for ammonia is low and it is not economically wise to have large losses.

Purge gas. A small portion of the overhead from the primary separator in the ammonia synthesis loop is taken as a purge to prevent the buildup of inerts in the circulating gas system. The purge gas is cooled or scrubbed to minimize the loss of ammonia and at some plants the purge gas is used as fuel in the primary reformer, in the boilers, or in nitric acid plants.

The amount of gas purged from the synthesis loop varies with the type of technology used at each plant. This gas contains around 62% hydrogen, 21% nitrogen, 4% argon, 11% methane, and 2% ammonia.

5.2.2 Ammonium Nitrate Plants. Ammonium nitrate production processes can emit particulates (NH_4NO_3 and coating materials), ammonia, and nitric acid. Nitric acid is not normally emitted unless the neutralizer is operating under acidic conditions. A more detailed analysis of emissions from unit processes follows.

Neutralizer. Emissions occur when steam is liberated during the exothermic neutralization reaction. Emissions of ammonium nitrate and ammonia occur as steam is vented from the neutralizer. EPA test results (7) indicated uncontrolled ammonium nitrate emissions to be 2.6 g/kg of NH_4NO_3 produced and ammonia emissions to be 18 g/kg of NH_4NO_3 produced.

Evaporator/Concentrator. The ammonium nitrate is concentrated from around 73 to 83% ammonium nitrate solution to 95 to 99% in the evaporator/concentrator. Emissions of ammonium nitrate and ammonia occur as the steam and air are vented from the unit process. Emissions from evaporators as reported by EPA (7) are

Ammonium Nitrate	0.03 - 0.07 g/kg NH_4NO_3
Ammonia	0.066 - 4.2 g/kg NH_4NO_3

Prill tower. Prill tower emissions result from the carryover of fine particles and fumes by the air exiting the tower. Fine particles originate from the formation of microprills and prill breakup. Fuming results from the dissociation of ammonium nitrate

and is proportional to melt temperature. The fume may recombine upon exiting the tower, forming submicron crystals. Tower airflow affects emissions - increased tower velocity increases the entrainment of particles. EPA (7) reports uncontrolled emissions from low and high density prill towers as follows:

	Particulate	Ammonia
Low Density Prill Tower	0.39 g/kg NH_4NO_3	0.13 g/kg NH_4NO_3
High Density Prill Tower	1.6 g/kg NH_4NO_3	28.6 g/kg NH_4NO_3

Granulators. Granulators require less air for operation than prill towers. The chilled air entering the drum granulator can entrain up to 10 to 20% by weight of product. In the case of pan granulators, there is little airflow over the pan; consequently, entrainment of fine spray or seed is less than that encountered in drum granulation. As with prills, a rapid change in crystal state can cause the granules to break up into dust. This dust can become entrained in the airstream from both types of granulators, increasing emissions. EPA test data (7) on uncontrolled emissions from granulators are as follows:

	Particulate	Ammonia
Drum Granulators	147.2 g/kg NH_4NO_3	29.7 g/kg NH_4NO_3
Pan Granulators	1.34 g/kg NH_4NO_3	0.07 g/kg NH_4NO_3

Predryer, dryers, and coolers. Precooling, cooling, and drying are usually conducted in a rotary drum using conditioned or ambient temperature air. Emissions consist of fine particulates and ammonia that have eroded from the product and become entrained in the discharged airstream. The airflow rate through the drum affects emissions; the higher the airflow rates, the higher the amount of fines entrained.

Because of low moisture content, high density prills only require cooling when they exit the prill tower, whereas low density prills with a higher water content are dried in three stages: predrying, drying, and cooling. These steps are normally conducted in three separate rotary drums. The results of EPA testing (7) indicate that particulate (NH_4NO_3) and ammonia are emitted at the following rates:

	Particulate (g/kg NH_4NO_3)	Ammonia (g/kg NH_4NO_3)
Low Density Predryer	10.1 - 37.3	0 - 0.29
Low Density Dryer	11.4 - 93.7	0 - 1.3
Low Density Cooler	12.3 - 37.8	0 - 0.29
High Density Cooler	0.83	0 - 0.03
Drum Granulator Cooler	7.5 - 8.6	0 - 1.2
Pan Granulator Precooler	18	0
Pan Granulator Cooler	0.25	0

Screens. Almost all screening operations used in this industry are enclosed or at least have a cover over the screens. Emissions that are generated by the attrition of the solids against one another and against the screens are normally vented to control equipment or from the building. Tests (7) indicated that this operation is a small emission source, and generally no visible emissions are observed.

Coater. Prills and granules are usually treated to prevent them from caking. In some cases, additives are injected into the melt or, alternatively, the solids are coated with kaolin, diatomaceous earth, or talc. Prills and granules are normally coated in a drum coater. The mixing action causes some of the coating material to be suspended in air. By keeping the drum under a slight negative pressure, the emissions can be vented to a control device. Uncontrolled emissions of particulate range from 0.5 to 3 g/kg NH_4NO_3 (7).

5.2.3 Urea Plants. Ammonia and particulates emitted per kilogram of urea produced for each unit process are discussed below based on information in the literature.

Reactor. Most solution processes have emission sources where inerts are vented; however, this unit process is not considered to be one of the major sources of air pollution for this industry. In the Stamicarbon CO_2 stripping process, gases containing NH_3 and excess CO_2 are vented through an NH_3 scrubber. In the SNAM PROGETTI process, two airstreams containing NH_3, CO_2, and urea are treated by water scrubbers.

Concentrator. A vacuum is maintained by a steam ejector on the crystallizer overhead vent. Minor emissions containing NH_3, CO_2, and water vapour pass through a condenser and then go to the atmosphere. The evaporators are also operated under a

vacuum using steam ejectors. Emissions are similar to those from crystallizers. The air-swept evaporators produce an airstream containing NH_3, CO_2, and urea particulates, which is normally recycled to process. Controlled emission levels from the solution concentration equipment are estimated to be 1.73 $\pm$ 0.64% g/kg urea for NH_3 and 0.11 $\pm$ 28% g/kg urea for particulates (8).

Prill tower. In the prill tower, ammonia is released from the degradation of urea to biuret and from excess ammonia still present in the urea melt. Particulate emissions are small urea droplets, formed during spraying, that solidify and leave the tower in the exiting gas. Uncontrolled emission levels from the prill tower are found to be 0.40 $\pm$ 84% g/kg urea for NH_3 and 3.2 $\pm$ 17% g/kg urea for particulates (8).

Granulator. Because up to 20% of the urea may be entrained in the cooling airstream from the granulator, scrubbers are always used in conjunction with granulators. Emissions from the scrubber are estimated to be 0.25 $\pm$ 48% g/kg urea for ammonia and 0.09 $\pm$ 29% g/kg urea for particulates (8).

Cooler, screen, and coater. At many plants, coolers are not required and only a small percentage of the urea produced is coated with kaolin and diatomaceous earth. The product is screened in a building housing the storage and bagging facilities. Emissions from solid product finishing, based on the amount of fines that can be entrained in the air, are estimated to be around 2.15 g/kg urea for particulate emissions and 0.12 g/kg urea for NH_3 emissions (8).

5.2.4 Ammonium Sulphate Plants. The only significant source of particulate emissions from the manufacture of ammonium sulphate is from the dryer. Fugitive particulate emissions from screening equipment and materials handling are not significant and will not be addressed.

Dryers. Rotary dryers are used in ammonium sulphate plants. The hot ammonium sulphate emission laden gases from the dryer are sent through a pollution control device. Uncontrolled ammonium sulphate emissions from the rotary dryers are found to be around 26 g particulates per kilogram of product (9).

5.2.5 Nitric Acid Plants. Tail gas from the absorption tower contains unabsorbed oxides of nitrogen. These oxides are largely in the form of nitric oxide and nitrogen dioxide. In addition, trace amounts of nitric acid mist are present in the gases.

Emissions from plants without waste gas treatment equipment ranged from 0.1 to 0.7 vol.% nitrogen oxides, with an average of 0.37 (10). Nitrogen dioxide accounts for 30 to 50% of these values, the balance being nitric oxide.

With the addition of a catalytic combustor, the data show that the total nitrogen oxides in the tail gas leaving the combustor were reduced by 35 to 99%. In all cases, the stack effluent was clear and colourless, indicating the reduction of all NO_2 to NO.

5.3 Emission Sources from Phosphate Fertilizer Plants

5.3.1 Sulphuric Acid Plants. The major source of emissions from the contact sulphuric acid plant is the waste gas from the absorber exit stack. Minor additional quantities of sulphur dioxide and sulphur trioxide are released from storage tanks, tank cars, acid concentrators, and leaks in the process.

5.3.2 Phosphate-Rock Grinding. The grinding of phosphate rock can send particulate emissions to the atmosphere, especially if the material is very dry. Dust can also be a significant problem at each point of transfer of the material, from the unloading area through to the fine rock storage silos.

After the phosphate rock enters the plant, flow-through sizing and reclamation circuits use pneumatic transfer means when dry grinding is performed. Air is continually being exhausted from the system to remove fine entrained rock particles. This air is normally vented through bag filters, which capture the fine dust.

5.3.3 Phosphoric Acid Plants. The calcium fluoride constituent of phosphate rock ore will react during acidulation to produce hydrogen fluoride as shown below. In addition, calcium fluoride will react with phosphoric acid to produce hydrogen fluoride.

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$
$$CaF_2 + 2H_3PO_4 \rightarrow Ca(H_2PO_4)_2 + 2HF$$

The hydrogen fluoride evolved may leave the slurry as a gas or it can react with any silica present in the rock to give

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

If the phosphoric acid is concentrated, fluosilicic acid (H_2SiF_6), which will be present in the acid solution, can dissociate to form

$$H_2SiF_6 \rightarrow SiF_4 + 2HF$$

The fluoride products formed can volatilize and are, thus, major emission species in the emission stream. Emissions of fluorides, acid mist, and particulates are evolved from the digester, filter, and other plant equipment. In the acid concentration step, some of the phosphoric acid along with minor acid impurities, such as fluorides, volatilizes with the water vapour. Fluosilicic acid can be recovered as a by-product, resulting in a 50% reduction in the average emission of fluorides.

5.3.4 Normal Superphosphate Plants. The major sources of emissions at a NSP plant are the mixer, den, and curing building. Calcium fluoride contained in the phosphate rock is attacked by the sulphuric acid, resulting in HF emissions. The HF will react with silica to form SiF_4 plus water. SiF_4 is also evolved through the denning operation and curing step. The mixer and den are essentially closed and fluoride, acid mist, and dust particles are collected and treated. Emissions from the curing building are also treated.

5.3.5 Triple Superphosphate Plants. As is the case of normal superphosphate, SiF_4 and HF are also evolved in the mixer and during denning, curing, and storing operations. As with NSP, the HF reacts with silica to form SiF_4, which partially hydrolizes to form fluosilicic acid and is partially evolved as a gas.

Granular NSP and TSP are produced by utilizing ground, run-of-the-pile material treated with water and steam in rotating chambers. This process does not produce significant emissions because the major portion of the fluorides was evolved in the original run-of-the-pile manufacture. Dust is evolved at the screens and crushing mill, which is collected and treated. Fluoride and dust emissions from the dryer are also collected and treated.

5.3.6 Ammonium Phosphate Plants. In the production of ammonium phosphate, air emissions originate from the following sources: reactor - ammonia and fluorides; granulator - ammonia, fluorides, and particulates; dryer - ammonia, fluorides, particulates, and combustion gases; cooler - ammonia, fluorides, and particulates; and screens and material transfer - particulates.

Ammonia emissions are a result of incomplete chemical reaction and excess free ammonia. Fluoride emissions originate from the fluoride content of phosphoric acid and consist primarily of silicon tetrafluoride. One hundred percent collection and scrubbing efficiencies are not attainable; thus, there are some fugitive and stack emissions. Screening and product transfer processes produce both fugitive and stack particulate emissions.

5.4 Air Emission Characteristics

The major emission problems associated with the production of phosphate fertilizers are fluorides, particulates, ammonia, sulphur dioxide, and acid mists resulting from specific processes. The following sections characterize the emissions associated with each product.

5.4.1 Sulphuric Acid Plants. Uncontrolled oxides of sulphur from the absorber could exceed 4.5 kg/t of acid produced. In fact, SO_2 emissions in the tail gas of old single-absorber uncontrolled plants may be as high as 14 kg/t H_2SO_4. Sulphur dioxide in the tail gas of plants employing double absorption amounts to approximately 0.5 kg/t H_2SO_4. In addition, acid mist emissions, if uncontrolled, could be as high as 3.7 kg/t of 100% acid (11).

Plants in Canada do not operate without emission control equipment; however, emissions could approach the uncontrolled level when scrubbers and precipitators break down or malfunction, or if catalytic beds are being used when they should have been replaced.

5.4.2 Phosphate-Rock Grinding. After the rock enters the mill, flow-through sizing and reclamation are by pneumatic means. Air is constantly exhausted via a bag filter to prevent the buildup of fines and the precipitation of moisture. Estimated dust emissions from rock unloading, grinding, sizing, and storing are 0.20 g/kg P_2O_5.

5.4.3 Phosphoric Acid Plants. Fluoride emissions from wet-process phosphoric acid will vary depending upon the type of rock used. Gaseous emissions consisting of hydrogen fluoride, silicon tetrafluoride, water vapour, and acid mist, as well as solid particles, are controlled through the use of wet scrubbers. Controlled emissions, with and without the recovery of by-product fluorine, as noted in the literature are (11)

Wet Scrubber System	Total F (g/kg P_2O_5)	Particulate (g/kg P_2O_5)
Overall	0.010 ± 47%	0.054 ± 164%
With Recovery of Fluorine	0.0059 ± 61%	-

5.4.4 Normal Superphosphate Plants. The reaction of phosphate rock with sulphuric acid forms HF, which reacts with silica in the rock to form SiF_4. This, in turn, reacts with water to form fluosilicic acid; however, some of the SiF_4 is volatilized before

reaction with water takes place. SiF_4 is also evolved through the denning operation and during the curing step. Emissions from NSP plants are as follows (11):

Source	Particulate (g/kg P_2O_5)	Fluoride (g/kg P_2O_5)
Rock Feeding*	0.055 ± 180%	0
Mixer and Den*	0.26 ± 86%	0.10 ± 120%
Curing Building**	3.6	1.9 ± 120%

* values are for controlled conditions
** values are for uncontrolled conditions

5.4.5 Triple Superphosphate Plants. Fluorides and particulates are released during the production of run-of-the-pile triple superphosphate and during the production of granular triple superphosphate. Estimated emissions from these two products are (11)

	Emission Factor (g/kg P_2O_5)	
	Particulate	Fluoride
Run-of-the-Pile TSP		
Rock Feeding	0.014 ± 170%	0
Mixer, Den, Curing	0.16 ± 50%	0.10 ± 40%
Granular TSP		
Rock Feeding	0.017 ± 180%	0
Reactor, Granulator, Dryer, Cooler, Screens	0.05 ± 320%	0.12 ± 30%
Curing Building	0.10 ± 240%	0.018 ± 40%

5.4.6 Ammonium Phosphate Plants. Air emissions from the equipment used in the manufacture of ammonium phosphate are (11)

Reactor:	Ammonia, Fluorides
Ammoniator-Granulator:	Ammonia, Fluorides, Particulates
Dryer:	Ammonia, Fluorides, Particulates
Cooler:	Ammonia, Fluorides, Particulates
Product Sizing and Transfer:	Particulates

Ammonia emissions are a result of incomplete chemical reaction and excess free ammonia. Fluoride emissions originate from the fluoride content of the phosphoric acid and consist mainly of SiF_4. Product sizing and material transfer process steps produce both controlled and fugitive emissions. Emission factors based on the literature are (11)

Source	Controlled Emissions (Mean Value, g/kg P_2O_5)
Reactor/Ammoniator-Granulator	
Fluoride	0.023
Particulate	0.76
Dryer/Cooler	
Fluoride	0.015
Particulate	0.75
Product Sizing and Transfer	
Fluoride	0.001
Particulate	0.03
Total ammonia emissions	0.068

6 SOLID WASTE SOURCES AND CHARACTERISTICS

6.1 Solid Wastes from Nitrogen Fertilizer Plants

Domestic and maintenance wastes, such as garbage, waste construction materials, old pipes, etc., from the fertilizer complex go to landfill sites.

6.1.1 Ammonia Plants. At some plants, zinc oxide beds are used for the desulphurization of the feed gas. This utilized zinc is either sold for reclamation of the zinc or placed in a controlled landfill site.

Spent catalyst must occasionally be replaced. These catalyst beds, which could be nickel, cobalt-molybdenum, chromium oxide - iron oxide, or copper oxide -zinc oxide based, are disposed of by a catalyst disposal/recovery company or should be disposed of in a controlled landfill site.

Raw water normally has to be treated to remove suspended solids and certain dissolved solids before it is demineralized for use in steam boilers. The sludge (such as carbonates, bicarbonates, hydroxides, silica, etc.) from the bottom of the clarifier is sent to a pond or landfill site. Solids present in boiler and cooling tower blowdown normally settle out in ponds.

6.1.2 Ammonium Nitrate Plants. There should not be any solid wastes generated in an ammonium nitrate plant. The dangers of combustion and explosion, when ammonium nitrate is handled, are well known. Combustion of ammonium nitrate is catalyzed by the presence of chloride, organic material, and some metals; thus, it is dangerous to recycle spilled contaminated material to the process. It may, however, be processed in a compound fertilizer plant where it does not pass through an evaporator and is diluted with other material.

6.1.3 Urea Plants. There should not be any solid wastes emitted from a urea plant. Any fines or spills are recycled to process. The occasional off-spec and solid spills from the sulphur coated urea plant are usually added to conventional fertilizer blends.

6.1.4 Ammonium Sulphate Plants. There should not be any solid wastes emitted from an ammonium sulphate plant. Any fines or spills are recycled to process. At one plant studied, the annual ammonium sulphate tank cleanings, which are mainly comprised of a mixture of zinc, ammonium phosphate, and sulphate, are sent to an old liming pit.

6.1.5 Nitric Acid Plants. There should be no solid wastes emitted from nitric acid plants.

6.2 Solid Wastes from Phosphate Fertilizer Plants

Domestic and maintenance wastes, such as garbage, waste construction materials, waste maintenance materials, and a small amount of spoiled fertilizer solids, go to landfill sites. Wood is often burned, plastics are buried, and metals normally go to scrap dealers.

6.2.1 Sulphuric Acid Plants. There should be no solid wastes emitted from sulphuric acid plants. Periodically, some spilled contaminated sulphur will go to a landfill site.

6.2.2 Phosphate-Rock Grinding. There should be no solid wastes emitted from the phosphate grinding circuit as spills and fines are recycled to process. If wet scrubbers are used for air pollution control, the fines settling out in the retention pond are reclaimed.

6.2.3 Phosphoric Acid Plants. Gypsum from the filtration of wet process phosphoric acid and sludge from the bottom of the clarifier are generated at wet phosphoric acid plants. These suspensions are sent to a pond where solids settle out. Gypsum, a by-product in WPPA manufacturing, is formed by reaction of phosphate rock with H_2SO_4. The slurry flows to a filter where the acid is drawn off by vacuum filtration, leaving the gypsum cake. The cake is washed and then slurried to a pond. If land is scarce, the filter cake is transported to piles. The quantity of gypsum produced in a WPPA plant ranges from 4.6 to 5.2 tonnes per tonne P_2O_5 produced.

Sludge, the second source of solid residue, results when impurity-bearing minerals settle out in the phosphoric acid clarifier to form acid sludges. Fluosilicates, fluorides, silica, cryolite, sulphates, unreacted rock, and various other complex salts form the sludge. Studies conducted at the University of Florida indicated that the highest ^{226}Ra concentrations were found in tank sediments and scale, i.e., about 0.81 Bq/g versus 0.48 Bq/g for phosphogypsum and 0.0074 Bq/g found in the acid. Acid sludge can be dried and used as a fertilizer filler or sent to the pond. The quantity of sludge ranges from 0.7 to 3.2 m^3/t P_2O_5 (11).

6.2.4 Ammonium Phosphate Plants. At ammonium phosphate plants, scrubber liquor contains about 10 kg of solid residue (mainly silicon hydroxide) per tonne P_2O_5. This solid residue is normally deposited in the gypsum pond.

6.2.5 Normal and Triple Superphosphate Plants. Scrubber liquor from both NSP and TSP plants will also contain solid residue that will settle out in the gypsum pond. There should be no other solid residues emitted from these plants.

7 WASTEWATER CONTROL AND TREATMENT TECHNOLOGY

A considerable effort has been made to eliminate or minimize most of the contaminants from fertilizer industry process effluents, which are particularly detrimental to natural water receiving bodies. Much of this work has been directed at correcting the source of the contamination or at in-plant process improvement rather than at end-of-pipe type treatment. A large part of the motivation for such improvement has been associated with the economics of the situation, i.e., improved operating efficiency and reduced costs. This section describes the general methods used by the fertilizer industry to control and treat liquid effluents.

7.1 Nitrogen Fertilizer Industry

This subsection deals with various approaches employed by the nitrogen fertilizer industry for controlling and treating liquid wastes. The different methods and processes available are briefly described.

7.1.1 Available Technology. Irrespective of the diverse products manufactured by this industry, the waste streams generated from these processes do not differ markedly; the major contaminants are ammonia and organic nitrogen. The methods used by the industry to control and treat contaminated process water can be divided into five general categories: disposal, process improvements and modifications, recycle and reuse, physicochemical treatment, and biological treatment.

Disposal. There are several methods of disposing of untreated and partially treated wastewaters: dilution, deep well injection, and ocean disposal. Dilution and deep well disposal were widely practiced until water quality standards became more stringent. These approaches are becoming increasingly unacceptable and will, therefore, not be discussed in this report.

Process improvements and modifications. The most feasible approach to water pollution abatement is to eliminate, reduce, or modify the sources of the wastewater. These basic principles result in improved process operations.

There are many ways in which these improvements can be made: alter the feedstock and products, modify the process, prevent spills and leaks, and recycle and recover valuable products.

Although these approaches may be relatively difficult to implement in an existing plant, their incorporation into the designing and planning of a new fertilizer

production facility is much easier. With present-day treatment costs and an environment-conscious world, considerable effort has been made by the industry to reduce the generation of waste streams.

A significant design modification, which has gained wide acceptance in the nitrogen fertilizer industry over the last few years, involves the use of centrifugal compressors rather than reciprocating compressors in both ammonia and urea plants. This changeover has resulted in reducing the oil contaminants in the waste streams from these plants.

Recycle and reuse. Recycling and reusing process waters can be an effective method of pollution abatement in an existing plant. The method is widely practiced within the fertilizer industry and at present a significant amount of the gross water requirements are supplied from recycled process waters.

Recycling of cooling water, steam condensate, and scrubber water is an accepted practice within the industry. This approach reduces operating costs and can also offer substantial savings in production costs by recovering chemicals prior to recycling. Recycling, however, usually generates a small, contaminated blowdown waste stream, which must be taken into consideration when reviewing the overall costs.

Various alternative schemes are currently being studied for recycling and reusing wastewater. One approach is to reuse process condensate, from the ammonium nitrate neutralizer, in a nitric acid absorber of a fully-integrated nitrogen fertilizer complex. This scheme shows considerable merit if the neutralizer is operated at a lower pH of 4 to 5. It would then reduce the chances of ammonia returning to the absorber, creating an explosion hazard. Lower neutralizer pHs, however, increase the potential for fire or explosive decomposition in the neutralizer pump tank.

Another recent scheme, which will be incorporated into the new ammonia plant at CIL Courtright, is based on 100% condensate recycling, utilizing a saturation tower to saturate natural gas feed going to the primary reformer with untreated condensate. This design utilizes the partial pressure of natural gas to facilitate saturation. All of the condensate is vaporized and serves as feed for the reformer.

Natural gas saturation has the following advantages: (1) elimination of additional reforming steam, (2) complete elimination of process condensate disposal, and (3) reduction in boiler feed water.

Physicochemical treatment. Several physical and/or chemical methods for treating the nitrogen fertilizer wastewaters are currently being used or are under

investigation. A summary of nitrogen fertilizer complex effluent treatment processes is shown in Figure 13.

Oil separators. American Petroleum Institute (API) oil separators are employed by the fertilizer industry for separating oil and grease from its waste streams. The sources of these contaminants are usually compressor blowdown, pump cooling water, and possibly condensates from ammonia plants. These streams are usually segregated from other wastes and sent to the API separators for removal of oil and grease. The oil-free water can then be mixed with other waste streams for further treatment or it can be discharged directly. After separation, the residual oil and grease levels in the wastewaters are expected to be less than 25 mg/L.

Design and operation of these separators has been carried out by the petroleum industry and is well documented (12,13). Because operation of these units does not pose any major problems to the fertilizer industry, further details have been excluded from this report.

Air stripping. Physical air stripping can be used to remove ammonia nitrogen from nitrogen fertilizer wastewaters. However, because of various drawbacks, this method has not been very successful in treating industrial wastewaters.

Ammonium ions in water exist in equilibrium with ammonia and hydrogen ions. As pH increases, the reaction equilibrium shifts, causing the release of ammonia. By increasing the pH, with lime, to above 10 and vigorously agitating the wastewater with diffused air, more than 85% of the ammonia can be released or stripped.

Ammonia removal efficiency depends on several factors, such as airflow rate, temperature, and concentration of wastes. At lower temperatures, the release of ammonia is depressed, so warm temperatures have to be maintained for effective stripping. Highly concentrated industrial wastes and municipal wastewater have successfully been treated by air stripping.

Most air stripping to date in the fertilizer industry has been with contaminated wastewater with less than 60 mg/L ammonia. By using the proper bed depth, the proper transfer medium, and the proper surface loading rate and with good control of pH, more than 90% removal of the ammonia is possible. Air stripping has been used successfully for ammonia-nitrogen removal from highly concentrated industrial wastes. However, the inherent drawbacks of this method are low removal efficiencies under low temperature conditions; ice formation in the stripping tower during winter operation; tower emissions can create significant air pollution; ammonia recovery is relatively difficult; any scale

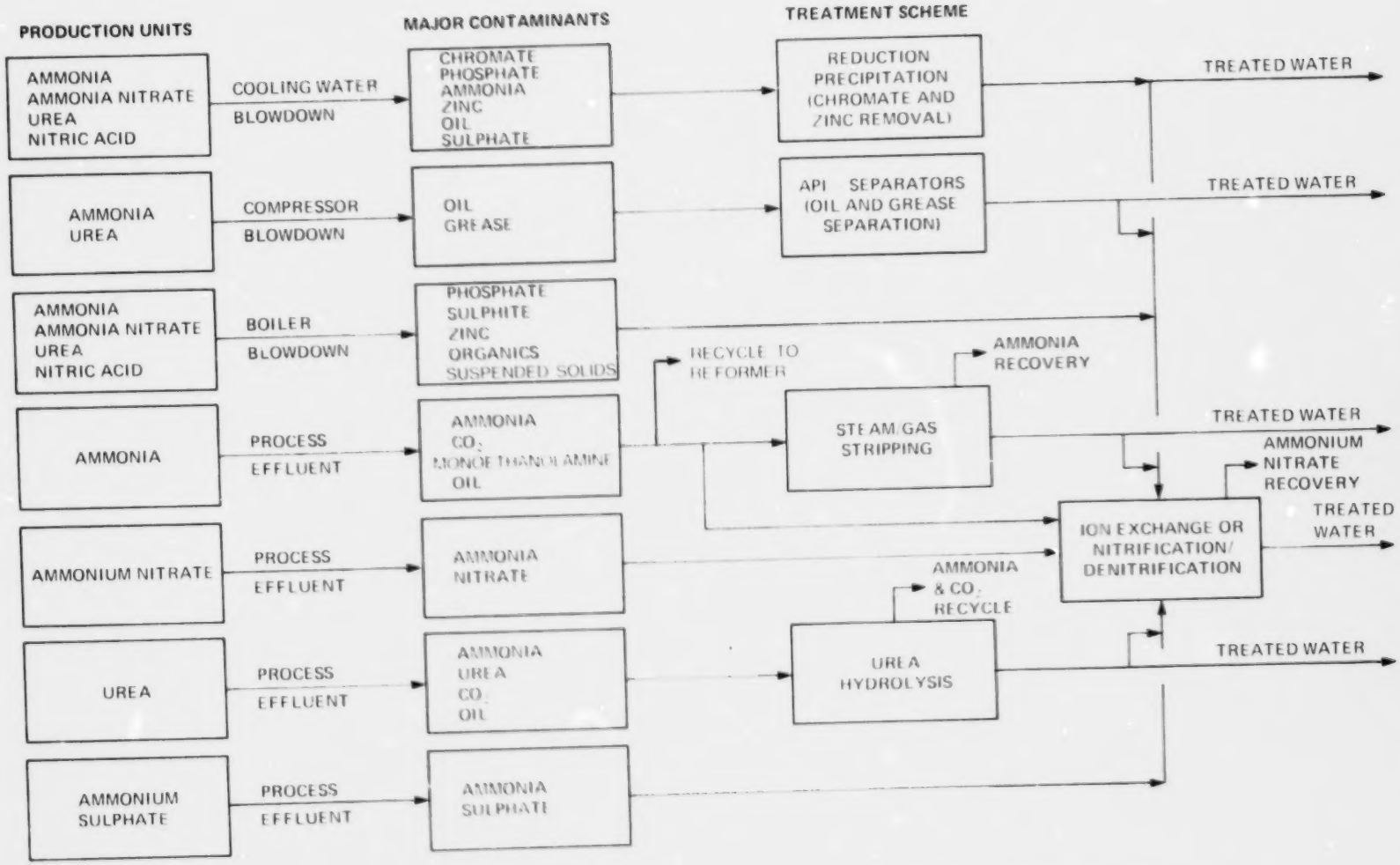


FIGURE 13 SUMMARY OF NITROGEN FERTILIZER COMPLEX EFFLUENT TREATMENT PROCESSES

formation minimizes tower airflow, thus reducing removal efficiency; oxidation of ammonia to nitrate; and ammonia released to the environment can be absorbed by water vapour and will reenter the process stream.

Contrary to some reports, cooling towers are not good stripping units for ammonia contaminated waters. Because of their construction and airflow, they are actually absorbers of airborne ammonia. As a result, their blowdowns may contain up to 50 mg/L of ammonia. A typical air stripping unit is shown in Figure 14.

Steam stripping. Steam stripping of ammonia has been used successfully at several nitrogen fertilizer plants. This method does not have the disadvantages of air stripping. It has the advantages of ammonia recovery and recycling. The major disadvantages of steam stripping are high steam costs, plugging of overhead lines with ammonium salts, and buildup of water in the recovered ammonia solution. However, allowing for high steam costs, the process can only be economical for high influent concentrations of ammonia (3 to 4%). Estimated steam consumption is two tonnes per five cubic metres of wastewater.

The basic chemistry of steam stripping is identical to that for air stripping and is generally carried out at pH levels greater than 10 to achieve greater than 95% ammonia removal. However, the ammonia nitrogen concentration in the effluent is normally 20 to 30 mg/L.

Lynch (5) has reported that steam stripping can remove more than 95% ammonia and methanol from ammonia plant condensate. However, two major drawbacks were encountered: high steam costs and the release of methylamines. To offset high steam costs, the majority of present stripping operations are operated in conjunction with ammonia recovery units.

Finneran and Whelchel (14) reported that steam was used to strip a mixture of 1000 mg/L ammonia, 2000 mg/L methanol, and carbon dioxide from ammonia plant process condensate. The stripper overhead was condensed for aqueous ammonia recovery and the ammonia, carbon dioxide, and methanol were reduced to 20 mg/L, 40 mg/L, and 50 mg/L respectively.

Kepple (15) described a system that recovers ammonia-nitrogen as ammonium sulphate and aqua ammonia by ammonia stripping with an absorption unit. This process overcomes the major disadvantages of conventional ammonia stripping, such as temperature limitations, ammonia discharge, etc. The wastewater is stripped at a pH greater than 11 and the ammonia gases are subsequently absorbed. The absorbent liquor is

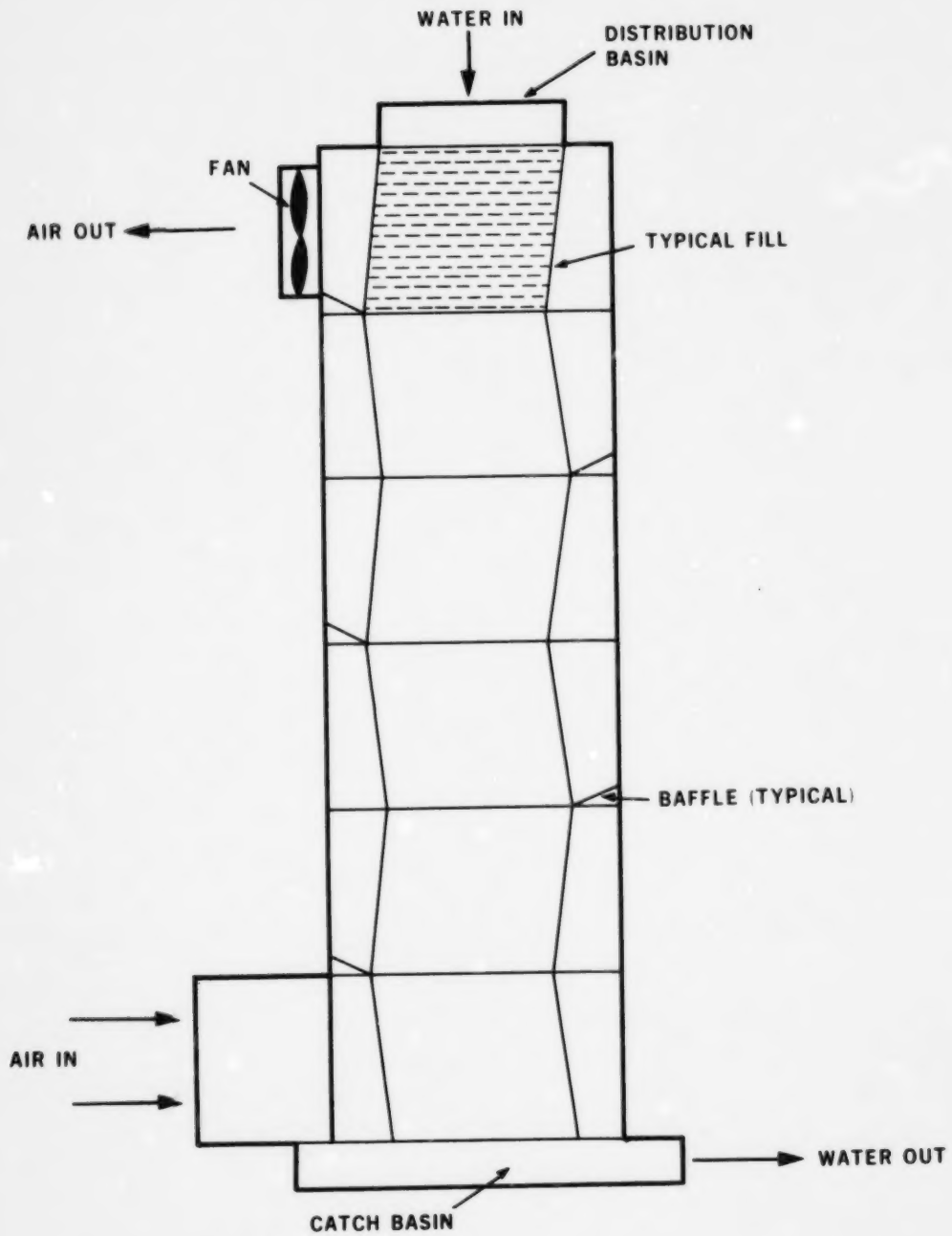


FIGURE 14 AMMONIA PROCESS CONDENSATE AIR STRIPPING UNIT

maintained at pH 6 for conversion to ammonium ions. The absorption unit can use either sulphuric acid, for ammonium sulphate by-product recovery, or steam to regenerate aqua ammonia. After gas stripping and subsequent water removal, the gas stream is recycled to the stripper.

A new process developed for the treatment of wastewaters in the petroleum industry can also be applied to fertilizer industry situations (16). The wastewaters are stripped by an inert gas and steam mixture and the overhead gas mixture flows to an absorber for ammonia recovery while the inert gas is recycled to the stripper. The use of a steam - inert gas mixture improves the overall efficiency of stripping, reduces operating costs, and prevents plugging. A typical steam stripping unit and also a steam-gas unit are shown in Figures 15 and 16 respectively.

Ion exchange. Ion exchange involves the exchange of ions of a given species from an insoluble exchange material with ions of a different species from a solution. This method has been used for many years in the water treatment field for the softening and conditioning of boiler waters.

In recent years, this method has increasingly been applied to industrial wastewater treatment due to the development of new natural and synthetic resins. Ion exchange technology is extremely well documented in the literature (17,18,19,20), especially with respect to its application to the fertilizer industry. It is possible to effectively remove the pollutant from the effluent and also to recover valuable by-products by using this method. Its application to the fertilizer industry is of special importance for the removal and recovery of both ammonium and nitrate ions; likewise for the removal and recycling of chromates from cooling water blowdown.

In ammonia recovery, positively-charged cations in the cationic resin bed are exchanged for wastewater ammonium ions to give a contaminant-free stream. The resin, holding the ammonium ions, slowly loses its exchange power and requires periodic regeneration, which is achieved by passing an acid solution, usually nitric acid, through the bed. Nitrate ions are removed with negatively-charged anion exchange resins that are then regenerated with alkaline solutions, usually ammonium hydroxide.

The use of ion exchange at Farmers Chemical fertilizer plant in the U.S. has been widely reported (21,22,23) and was chosen after careful evaluation of various alternative treatment methods. Influent ammonia/nitrate concentrations to ion exchange columns were 340 and 1240 mg/L, respectively, which were reduced to less than 3 mg/L of ammonia and 7 to 11 mg/L of nitrate. Other ions were also removed completely.

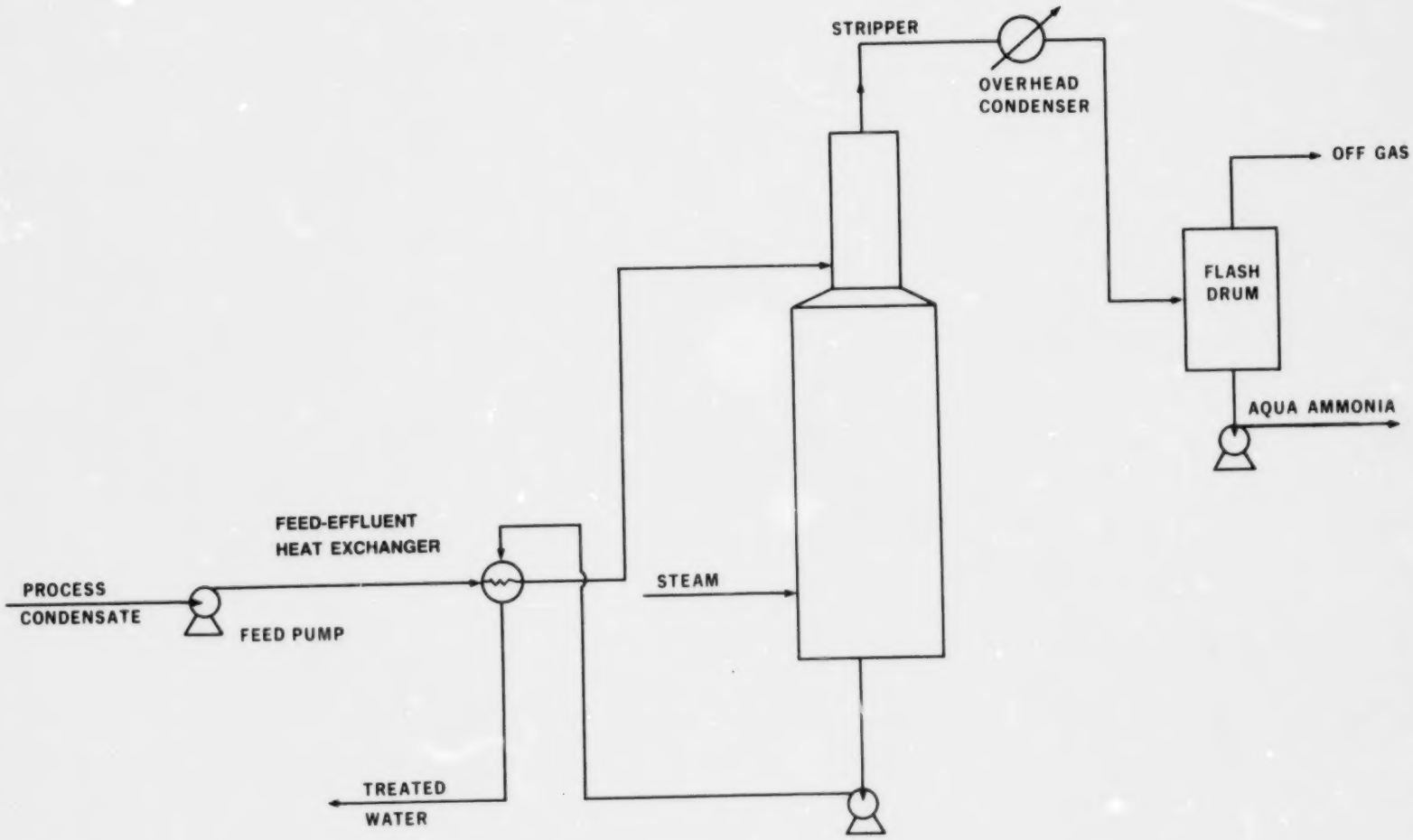


FIGURE 15 AMMONIA PROCESS CONDENSATE TREATMENT STEAM STRIPPER UNIT

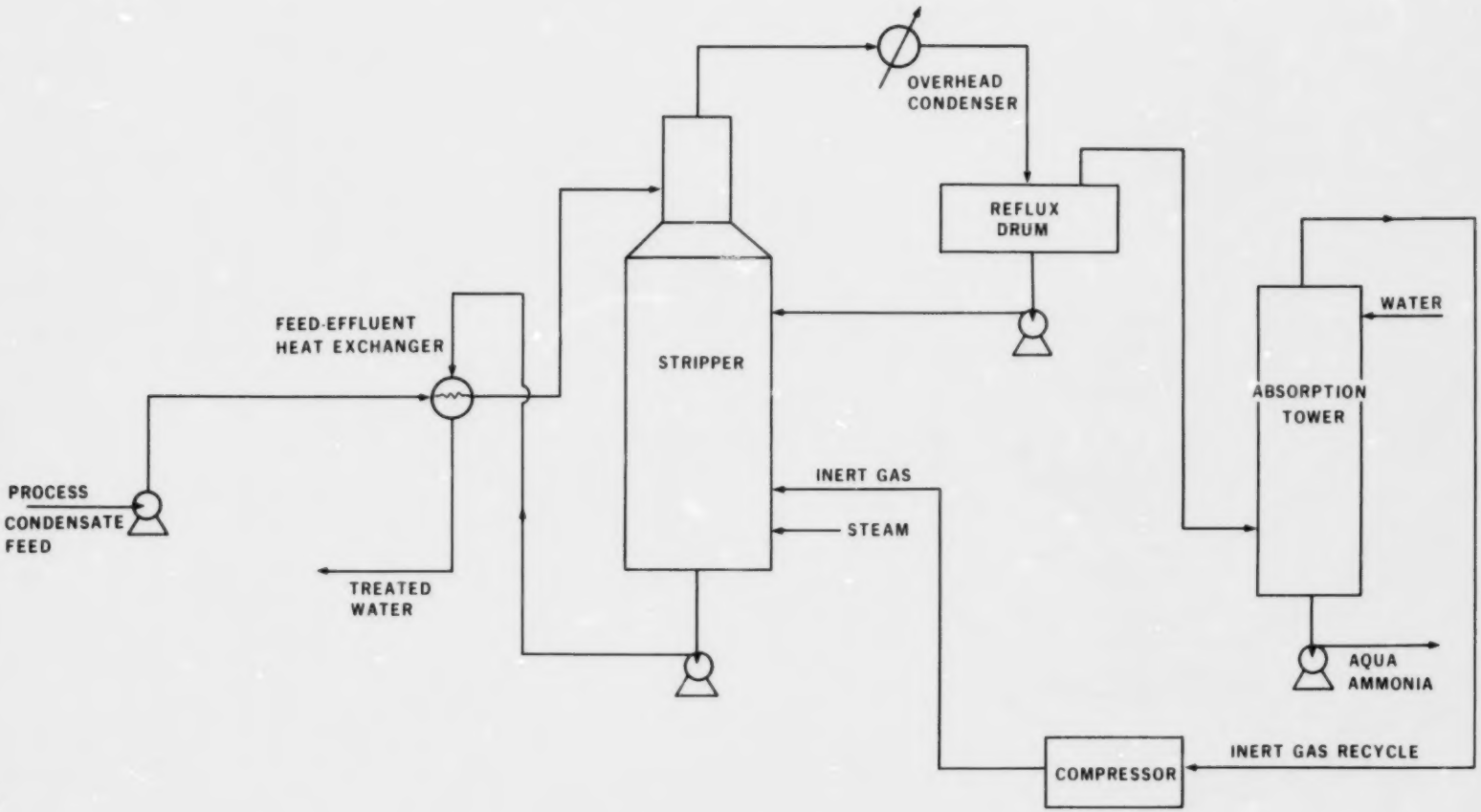


FIGURE 16 AMMONIA PROCESS CONDENSATE TREATMENT INERT GAS - STEAM STRIPPER UNIT

In Canada, ion exchange has been successfully demonstrated at the CIL plant in Courtright, Ontario (5). A cocurrent conventional cation exchanger unit with two exchange columns removes ammonia from the ammonia condensate stream. Ten percent sulphuric acid is used as regenerant. The ammonium sulphate solution from regeneration is recycled to the phosphoric acid plant. Ion exchange almost removes all the influent ammonia (700 mg/L) and amine compounds (25 mg/L) to effluent levels of less than 1 mg/L. In addition, about 95% of the ammonia and sulphuric acid regenerant is recovered in the phosphate process.

Ion exchange has also been used for polishing purposes in an ammonia plant (14), where the process condensate was steam-stripped and then sent to cation exchange to remove the majority of ammonia, organic materials, and metals. The treated water was then used as boiler feed.

The main advantages of ion exchange are good removal efficiencies, reliability, recovery of contaminants and regenerants, and feasibility of water reuse. High capital and operating costs and regeneration difficulties are its major disadvantages. However, the advantages outweigh the disadvantages and this method appears to have good potential for fertilizer process wastewater treatment. A typical ion exchange treatment scheme is shown in Figure 17.

Containment and recovery. Nitrogen-containing effluents from the ammonia, urea, and ammonium nitrate plants, including the process condensate from the low temperature CO shift converter and methanator, are collected and held in a containment area. The solution is pumped from this area to heat exchangers in the ammonia plant to heat the weak nitrogen-containing effluents with waste heat. The hot weak solution flows down through a packed-air-swept concentrator where the solution is raised from its initial, approximately 5% ammonium nitrate concentration to a 70% solution. After some adjustments, this solution is sold as a liquid fertilizer.

Nitrogen recovery using evaporation by mechanical vapour compression. Another system similar to the one above, which is presently being researched in Canada, collects nitrogen-containing effluents from ammonia fertilizer plants and concentrates the nitrogen-containing solution from around 3%, using vapour recompression-spray-film evaporation to preconcentrate the liquor, to 50%. A forced circulation finisher concentrates the liquor up to 85 to 92%.

In this Aqua-Chem unit, the feed is preheated by the distillate leaving the unit and is fed to the evaporation body. The steam generated in the evaporator body is

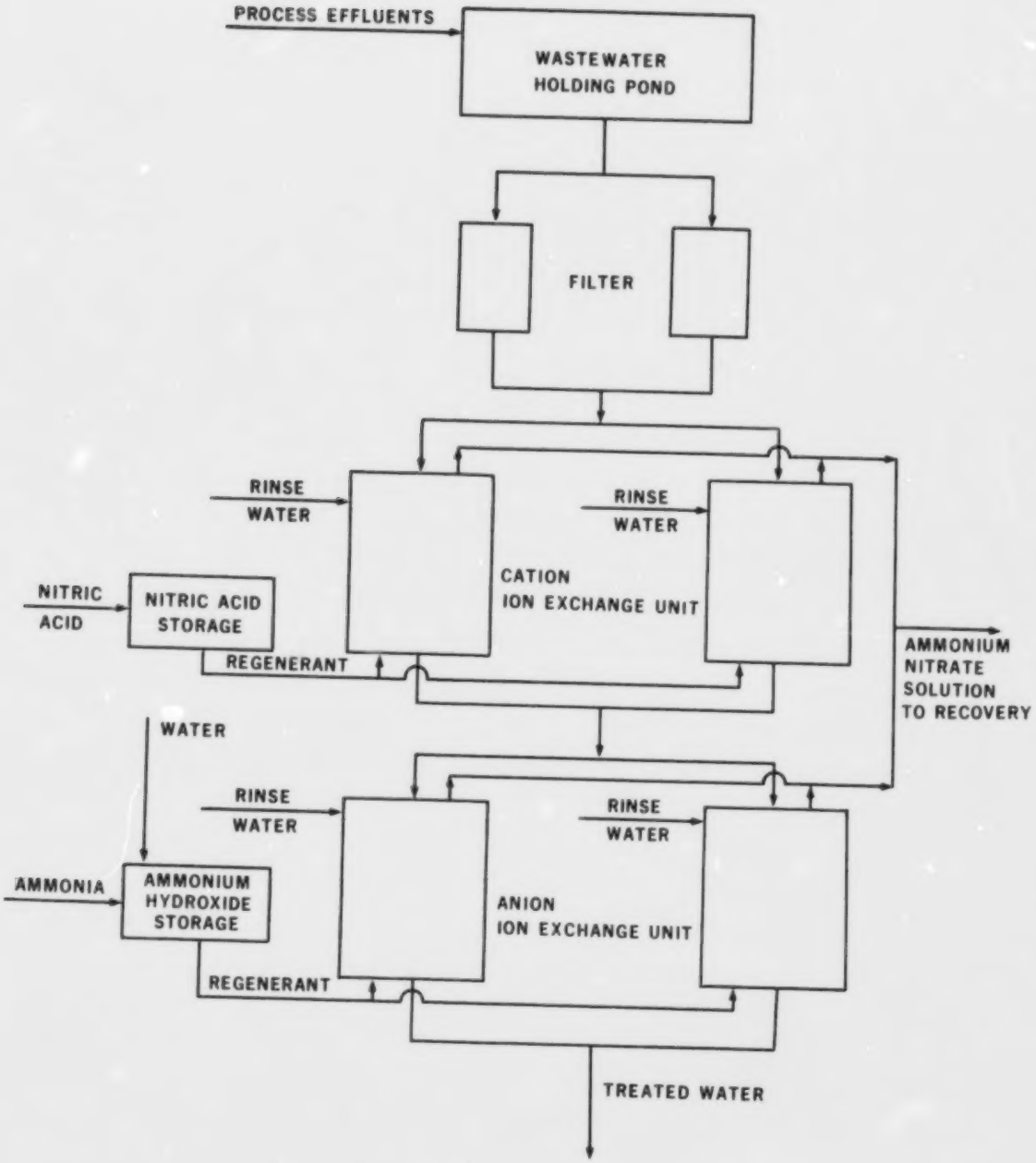


FIGURE 17 NITROGEN FERTILIZER COMPLEX PROCESS EFFLUENT TREATMENT - CONVENTIONAL COUNTERCURRENT ION EXCHANGE UNIT

compressed by a 1.119×10^6 W compressor from a gauge pressure of 135.4 to 205.6 kPa and returned to the tube bundle, thus providing the energy input to the evaporation process. The compressed steam gives its latent heat to the water to be evaporated and, in turn, is partially condensed. In this phase, the ammonium nitrate solution will reach a concentration of about 50%. The uncondensed portion of the steam is used in the forced circulation final concentrator, which operates at a gauge pressure of 33.8 kPa. The final concentration of the ammonium nitrate solution will be 92%. This concentrated solution will be used in the manufacturing of nitrogen fertilizer solutions. The distillate leaving the plant can be used in the demineralized water system, subject to its quality.

Chlorination. For many years, break-point chlorination has been used for the removal of nitrogen compounds from drinking water supplies. To date, however, this process has not been successfully applied to the treatment of fertilizer industry wastewaters due to the high chlorine requirements, large quantities of electricity required, chlorination of the organic content in wastewater, and generation of chloride content in the effluent. Because this method does not have any potential use within the fertilizer industry, it will not be discussed further in this report.

Miscellaneous methods. A scrubber unit has been developed for fertilizer plants to remove stream pollutants for by-product recovery (24). This unit is installed in the neutralization area of a continuous ammonium nitrate operation and the processing waste heat is used for heating an airstream containing entrained fertilizer solids. The air releases its solids and is then subjected to sequential evaporation and condensation to give a stream completely free of fertilizer.

Another alternative method, urea hydrolysis, has been developed for the treatment of process condensate from urea plants. In the thermal hydrolysis process, a single tower is used for both hydrolysis and desorption. Heated urea process condensate is fed directly to the stripping tower where dissolved urea is hydrolyzed to ammonium carbamate and the ammonium carbamate is decomposed to gaseous ammonia and CO_2, which exit overhead. This process is carried out at temperatures above 100°C and under pressures of up to 1.8 kPa. A few of these units are currently in operation in the U.S. In one of these installations, the generated effluent streams contain less than 200 mg/L urea and 50 mg/L ammonia (4).

Electrodialysis, reverse osmosis, and distillation are other treatment methods that are capable of 98% nitrogen removal efficiencies (17). These processes have many overall operating problems and are relatively expensive. Only reverse osmosis has been

given any serious consideration by the fertilizer industry for treatment of its wastewaters.

Chromate removal. Chromate-contaminated cooling water blowdown is usually treated separately from other process wastes or pretreated before combining it with other waste streams. The cooling tower blowdown can contain up to 200 mg/L chromate (as hexavalent chromium), which can be treated in a two-stage process of reducing the chromium ion followed by precipitation.

Reduction is carried out either with sulphur dioxide or sodium metabisulphite to convert the hexavalent chromium to its trivalent form under acidic conditions (pH 2 to 3). The reaction is allowed to take place in a tank or open pond for about 10 minutes. The final stage involves addition of a base, usually lime, to increase the pH to 8 to 9. The precipitate, so formed, is allowed to settle in a clarifier and its overflow is either discharged or mixed with other effluent streams. Chromium levels in the effluent achievable by this method are 2 mg/L or less. The process is shown in Figure 18.

Landy (25) has described the use of this method for a Saudi Arabian fertilizer plant. Metabisulphite was used as the reducing agent with lime as a coagulant. A retention time of 3 minutes achieved a chromate reduction from 70 mg/L to 0.5 mg/L.

Ion exchange is a possible treatment alternative but to date this has not been considered by the fertilizer industry. However, it has good potential because of savings in chemicals and operating costs and the possible recovery and recycling of the chromate.

An electrochemical chromate removal unit has been developed by Andco that has been used by fertilizer plants for removing chromate.

Using the low-chrome system in cooling towers, the blowdown will contain approximately 5 mg/L Cr^{+6}, which when mixed with other effluents can lower the concentration level to 0.15 mg/L, as is done in at least one of the plants studied.

Biological treatment.

Nitrification and denitrification. Biological nitrogen removal is essentially a two-step process, nitrification followed by denitrification. In the nitrification step, under aerobic conditions, autotrophic nitrifying organisms oxidize ammonia to nitrate. In the denitrification step, nitrate is reduced to nitrogen by heterotrophic organisms in the absence of molecular oxygen.

A considerable amount of work has been carried out on the evaluation and development of this nitrification-denitrification treatment method. The nitrification-

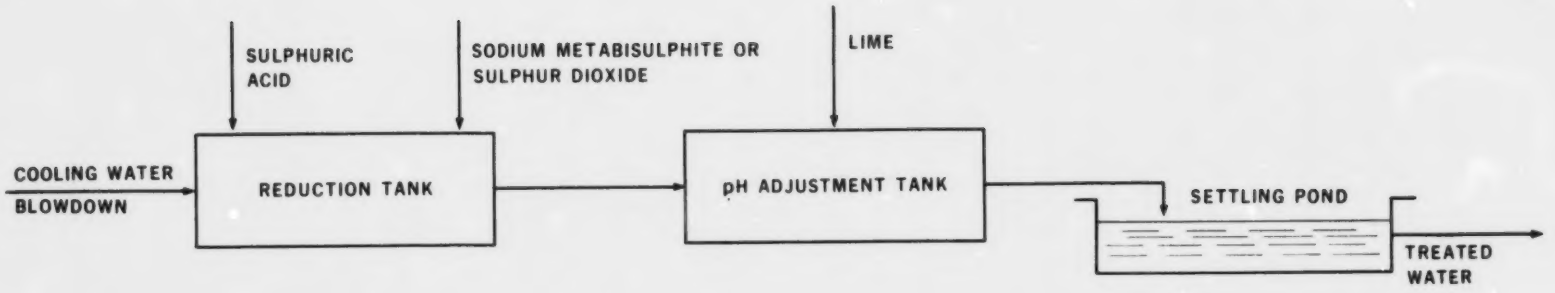


FIGURE 18 COOLING WATER BLOWDOWN TREATMENT - CHROMATE AND ZINC REDUCTION

denitrification treatment process, although used fairly extensively in municipal wastewater treatment, probably is not suitable for the nitrogen fertilizer industry in Canada. Its main disadvantages are low removal efficiencies, the low influent ammonia-nitrogen concentration required, temperature sensitivity, the adverse effects of wastewater toxicants, the release of sulphide odours, large land requirements, and the low influent organic carbon level.

Algae harvesting. Algae are multicellular forms of life, higher in order than bacteria. Their harvesting can be used for nitrogen removal. In areas where low cost land is readily available, aerobic lagoons can be utilized to convert ammonia nitrogen and phosphorus into algae. The biological cells are then removed from the treated wastewater. This treatment can remove 60% nitrogen but it has as drawbacks large land requirements, the difficulties related to algal cell harvesting, influences of temperature, and low removal efficiencies (17).

7.1.2 Water Pollution Control Measures. This section deals with various methods used by the Canadian nitrogen fertilizer industry for controlling and treating its liquid wastes. Existing effluent treatment methods are summarized in Table 14 and Table 4 shows the major contaminants discharged to water bodies from nitrogen fertilizer plants in Canada.

In-plant control measures. As mentioned earlier, the most feasible approach to water pollution control is to eliminate, reduce, or modify the sources of wastewater. There are many approaches, such as process modification, recycling and recovering valuable products, and preventing spills and leaks, by which the generation of waste streams could be reduced. Although these methods may be relatively difficult to implement in an existing plant, considerable effort has been made by the industry to reduce wastes. The approaches taken by various plants are included in Table 14.

All nitrogen fertilizer plants have taken steps to reduce wastewater discharges and contaminant loadings. In-house methods adopted include conventional approaches as well as many of the most recent technological advances. The following summary includes many of the techniques used by at least one of the plants in Canada.

1) Process condensate from the ammonia plant is treated by ion exchange. The resulting water stream is pure enough to be discharged to a receiving water body or used as boiler feed water or cooling tower makeup.
2) Condensate removed from the ammonium nitrate neutralizer tail gas is used in the manufacture of nitrogen solutions.

TABLE 14 WATER POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS

Plant	Ammonia Plant Process Effluent	Ammonium Nitrate Process Effluent	Urea Plant Process Effluent	Cooling Tower Blowdown
CIL, Courtright	Process condensate from the ammonia plants is treated by ion exchange before being discharged to the river. The ammonium sulphate recovered is consumed in the phosphoric acid plant.	Condensate removed from the neutralizer tail gas is used in the manufacture of nitrogen solutions. Floor washings and contaminated water from the ammonium nitrate prill plant are used as nitrogen solution make-up water.	Pump seal water is used for the manufacture of nitrogen solutions.	NA
Cyanamid of Canada, Niagara Falls	Process condensate from the ammonia plant goes to the steam generator. Any spills or washdown containing nitrogen and condensate from the ammonia synthesis loop are collected and concentrated to make liquid fertilizer.	Condensate removed from the neutralizer tail gas is used in the nitric acid absorber unit. Floor washings, spills, etc. that contain nitrogen are collected and concentrated to make liquid fertilizer.	Filtrate from the crystallizer is sent to the liquid fertilizer system. Wastewaters from vents, seals, compressors, storage facilities, spills, etc. also go to make liquid fertilizers.	A three cell Andco chromate removal unit and appurtenances was installed to treat cooling tower blowdown from the three cooling towers in the plant to meet objectives for chromium wastes.
Nitrochem, Maitland	Process condensate from the water scrubber (after the low temperature shift) is recycled to the reactor and high temperature shift unit. Blowdown from the hydrogen generator, caustic scrubber, water scrubber, and caustic wash goes to the equalization basin.	Condensate removed from the neutralizer tail gas is steam stripped to remove ammonia and then discharged to the sewer. Spills, leaks, and washups from this area go to the sewer and, thus, to the equalization basin. The stripper overhead is condensed for aqueous ammonia recovery.	NA	Because of blowdown chromate limitations, the cooling tower was changed to the Dearborn polyphosphate system.
Canadian Fertilizer Ltd., Medicine Hat	Process condensate from the ammonia plant is steam stripped to remove ammonia and methanol. The overheads go to the base of the reformer stack. The stripped condensate is recycled to the demineralizers.	NA	Process condensate from the urea plant is treated with ammonia plant condensate.	Cooling tower blowdown is sent to an equalization basin. The overflow goes to a river.
Cominco Ltd., Calgary	Process condensate from the ammonia plant is used for boiler make-up water.	Condensate removed from the neutralizer tail gas goes to the weak liquor tank as does the bleed-off from the wet cyclone (dryer scrubber). Barometric condenser water (evaporator) goes to the sewer.	Any condensate goes to the weak liquor tank as does scrubber effluent. A water purge from the mono-ethanolamine system goes to the sewer.	NA
Cominco, Carseland	Process condensate is steam stripped to remove NH_3 and methanol. The overheads go to the base of the reformer stack. The stripped condensate is reused for cooling water makeup or demineralizers. Spills, leaks, etc. go to the irrigation pond.	NA	Process condensate from the evaporators containing 2% NH_3, 20% CO_2, and 2000 ppm urea goes to the condensate steam stripper. The overheads are reclaimed. The treated condensate is used in the granulator scrubber. Spills go to the irrigation pond.	Cooling tower blowdown goes to the irrigation pond.

Oil Removal	Freshwater Treatment Plant Effluent	Boiler and Compressor Blowdown	Miscellaneous
Oil removed from process streams or spent lubrication oil is collected in drums. This oil is burned in the powerhouse or removed from the site by a waste disposal firm and incinerated.	All water required in the plant, apart from the once-through cooling water, is filtered and chlorinated. Some process water and boiler makeup is demineralized by the ion exchange technique. The regenerants are discharged to the sewer.	Discharged with cooling water.	Sanitary sewage goes to a total oxidation sewage disposal system, then to a river. Storm water is collected in a ditch system and joins the main effluent stream.
A skimmer is used to remove oil from effluent from the ammonia and urea plants.	Waste sulphuric acid from the ion exchange units is neutralized with lime, sent to a settling pond, and the clear effluent is decanted to the river. The solids resulting from the treatment of raw water with lime and iron sulphate settle in a pond.	The blowdown is discharged to a creek via a settling pond.	Sanitary sewage goes to septic tanks and tile fields. Storm water is collected in a ditch system and is discharged to the sewer.
Oil is removed from the condensate produced in the syn loop using an oil separator. The oil is burned or removed by a waste disposal firm.	River water is filtered and chlorinated. Some process water and boiler water is demineralized by ion exchange techniques. The units are regenerated using NaOH and H_2SO_4. The regenerants are discharged to the sewer.	The boiler and compressor blowdown is sent to an equalization pond that overflows to a river.	Sanitary sewage goes to the sewer. Storm water that does not join the main effluent flow goes to a stream.
Oil is removed from all process effluent using a belt separator. The oil is burned or removed from the site by an authorized firm.	Raw water is treated to remove solids and some impurities. The clarifier blowdown goes to the sludge basin. The clear effluent from the sludge basin goes to the equalization pond. The cation, anion, mixed bed, and polishing regenerants go to the equalization basin.	Boiler and compressor blowdown goes to the equalization pond.	Sanitary sewage goes to the sewer and, thus, to the equalization basin. Storm water is separated and goes to the evaporation pond.
The waste oil is burned on-site. Very little oil is present in the water effluent.	Lime, sodium aluminate, and soda ash are added to river water. The sludge goes to the sewer. The supernatant passes through anthracite filters, zeolite softeners, and a deaerator where polyphosphate and sodium nitrate are added.	Boiler and compressor blowdown goes to the sewer.	Sanitary sewage goes to a septic tank and tile field. Because of the porous nature of the soil, storm water soaks into the ground.
Decanted off wastewater ponds.	Raw water treatment effluent goes to the evaporation pond.	Boiler and compressor blowdown goes to the irrigation pond.	Sanitary sewage goes to the evaporation pond. Storm water is separated and part goes to the evaporation pond and part to a stream.

TABLE 14 WATER POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS (Cont'd)

Plant	Ammonia Plant Process Effluent	Ammonium Nitrate Process Effluent	Urea Plant Process Effluent	Cooling Tower Blowdown
Cominco, Trail	Process condensate containing about 150 mg/L NH_3-N goes to the sewer. About 32 000 m^3/d of reclaimed water from the ammonia and syn plant goes to the ammonium sulphate and phosphate plant. Process spills and wash waters are part of the reclaimed water.	NA	NA	There is no cooling tower blowdown.
Esso Chemical, Redwater	Process condensate is returned to the process or is used for boiler feed water. Leaks, spills, washdown, etc. can be discharged to the river via the settling pond or to the injection well via the retention pond.	Condensate from the neutralizer is reused in the plant. Washdown and leaks from the plant can go to the river via the settling pond or to the injection well via the retention pond.	Condensate is reused in the process. Wastewater from the ejector (on the evaporator), containing NH_3, CO_2, and water vapour, is sent to the retention pond.	All cooling tower blowdown goes to the river via the settling pond.
Western Co-op Fertilizers, Calgary	The process condensate is recycled to the utility plant for boiler feed make-up (without treatment). Other process effluents, such as leaks, spills, etc., go to a pond prior to final discharge to a river.	Process condensate, resulting from the vapour from the neutralizer passing through a fume scrubber and condenser, goes to the sewer. Spills, leaks, etc. go to the sewer.	NA	Cooling tower blowdown flows to a pond where solids settle out and pH adjustments are made prior to final discharge to a river. Chromate in the cooling water has been reduced.
Western Co-op Fertilizers, Medicine Hat (The ammonia plant is the only section currently operating.)	Process condensate goes to the boiler house without treatment. Other process effluents, such as leaks, spills, washup water, etc., go to the gypsum pond.	Process condensate is reused in the process. Spills, leaks, washup water, etc. that cannot be reused are sent to the gypsum pond.	NA	Cooling tower blowdown goes to the gypsum pond. Chromate in the cooling water has been reduced.
Sherritt Gordon, Fort Saskatchewan	Process condensate from the low temperature shift converter and methanator is primarily recycled as boiler feed water. The remainder is sent to a sewer. The condensate removed in the amine reflux drum is pumped back to the system.	NA	The process stream from the second-stage rectifier passes through a flash drum. Condensate from the flash drum and crystallizer condensers goes to a water supply tank. This water is subsequently put through the ammonia absorber-desorber system, which recovers ammonia returned from the scrubbers. The flashed vapours from the crystallizer are condensed and go to the water supply tank. Spills, leaks, washdown, etc. go to a holding pond.	Cooling tower blowdown is discharged to the river without treatment.
Simplot Chemical, Brandon	Process condensate is partially recycled for quench cooling. The remainder of the process condensate and other wastewaters high in nitrogen, such as spills and leaks, is recovered in the solutions plant.	Process effluent (condensate, spills, etc.) is recovered in the solutions plant.	The wastewaters are recycled to the solutions plant.	Cooling tower blowdown is discharged to the river during winter and is used for irrigation during the summer (May 15 to September 15).

Oil Removal	Freshwater Treatment Plant Effluent	Boiler and Compressor Blowdown	Miscellaneous
None. Compressor blowdown goes to the sewer.	There is no water treatment plant because of the softness of the river water. The water is only chlorinated.	Boiler and compressor blowdown containing about 150 mg/L NH_3-N goes to the sewer.	Sanitary effluent goes to the sewer. Storm water runoff goes to the sewer. Condenser water serving the $(NH_4)_2SO_4$ crystallizer goes to the sewer. Part of the scrubber solution in the $(NH_4)_2SO_4$ plant goes to the sewer.
No information available.	Raw water treatment solids go to the settling pond. The demineralizer regenerants go to the retention pond.	Boiler and compressor blowdown goes to the river via the settling pond.	Sanitary effluent can go to the injection well, the river, or may go off-site to a lagoon. Storm water can go to the river directly or via the settling pond. Some of the storm water can be diverted to the injection well via the retention pond.
Oil is removed from effluents by flotation in a holding pond.	There is no treatment plant. River water is sent to a pond to settle solids prior to usage.	Boiler and compressor blowdown goes to a pond prior to final discharge to a river.	Sanitary effluent from septic tanks flows to the same pond as other effluents. Storm water flows to a field.
No information available.	All water required in the plant is filtered and chlorinated. The sludge goes to the gypsum pond.	Boiler and compressor blowdown goes to the gypsum pond.	Sanitary effluent goes to septic tanks. The overflow goes to the gypsum pond. Storm runoff goes to a pond south of the plant. Some will go to the gypsum pond.
In the synthesis section, make-up gas is passed through an oil separator for removal of compressor lubrication oil and mixed with recycled syn gas. The oil is burned or removed from the site by an approved hauler.	Raw water treatment solids and demineralizer regenerants go to the river.	Boiler and compressor blowdown goes to the river without treatment.	Sanitary effluent from septic tanks flows to the river. Storm runoff is collected in open ditches and flows to a collection pond. The overflow from the pond goes to the river.
Oil in the final effluent is removed to below the 1 µg/L level by an oil separator.	The effluent from the demineralizers contains high amounts of ammonia and nitrates. This effluent is sent to a holding pond and is used for irrigation during the summer.	Boiler and compressor blowdown is discharged to the river during winter and is used for irrigation during the summer.	Sanitary effluent goes to the city sewage treatment plant. Storm water is separated and goes to the river or to the irrigation pond during the summer.

3) Part of the effluent stream from the condensed ammonium nitrate neutralizer exhaust is used as a feed to the absorption column in the adjacent nitric acid plant.

4) Pump seal water from the urea plant is used for the manufacture of nitrogen solutions.

5) Floor washings, spills, leaks, etc. from the ammonia, ammonium nitrate, and urea plants are used for the manufacture of nitrogen solutions.

6) Process condensate from the ammonia and ammonium nitrate plants is steam stripped. The resulting water stream is used as boiler feed water or cooling tower makeup or is discharged to a receiving body.

7) Wastewater containing nitrogen and other wastes, such as blowdown, is used for land irrigation during the summer and goes to a receiving water body during the winter.

8) Untreated process condensate from the ammonia plant will be used to saturate the natural gas feed going to the primary reformer.

External control measures. Liquid effluent systems in the nitrogen fertilizer industry are, of course, designed to ensure compliance with environmental requirements, but must also take into account factors unique to the individual plant site - its component manufacturing units and their process effluents, annual precipitation and surface runoff, sanitary water disposal, on-site disposal and recycling opportunities, characteristics of the surrounding area, and the volume, flow, and downstream considerations of nearby rivers or other water bodies. Systems currently in use range from complete on-site disposal to discharges, of about the same volume as freshwater intake, to nearby water bodies.

Most of the nitrogen fertilizer plants are component units of complexes that include the manufacture of phosphate fertilizers and, to a lesser extent, other industrial chemicals. Final effluent, therefore, will contain a combination of wastewaters from a number of sources.

Wastewaters are directed to settling ponds, evaporation ponds, gypsum ponds, and deep wells and, where practical, they are used for the irrigation of nearby farmlands, thereby minimizing or eliminating discharge to water bodies. In a number of cases, condensates are used in other plant processes, further reducing off-site discharge. Sanitary wastewater is discharged to septic tanks and tile fields in most cases. One plant has a total oxidation sewage system. Storm water is segregated in some plants but there are plants where it joins the main effluent discharge and ends up at the same discharge point.

With the many in-plant control measures taken at nitrogen fertilizer plants, the final effluent does not require elaborate external treatment systems to meet environmentally acceptable levels. Several ammonia and urea plants have oil removal systems and a few plants have pH control and settling ponds for suspended solids removal, but in most cases this is not a problem.

7.2 Phosphate Fertilizer Industry

This section deals with the various methods employed by the phosphate fertilizer industry for controlling and treating liquid wastes. A brief description of these treatment technologies is given. Figure 19 summarizes the various effluent treatment processes of the phosphate fertilizer complex.

7.2.1 Available Technology. The main production processes in this industry are phosphoric acid, normal and triple superphosphate, diammonium phosphate, and sulphuric acid. The liquid wastes generated during the manufacture of these products do not pose any unusual problems and, with present-day technology, zero pollutant discharge can be achieved. In fact, in the majority of the phosphate fertilizer complexes, a significant amount of the gross water requirements is met by recycling contaminated water. Thus, the net water requirement of the phosphate fertilizer industry can be reduced to negligible quantities, allowing for make-up and unusual operative situations.

The control and treatment methods employed by this fertilizer industry are categorized as follows: disposal, process improvements and modifications, recycle and reuse, physicochemical treatment.

Disposal. Disposal entails discharge of these untreated industrial wastes into receiving waters, which in most cases under present environmental conditions is not permitted due to their fluoride and phosphate contents.

Ocean disposal is used to a limited extent in the phosphate fertilizer industry. It is essentially a variation of disposal by dilution. As such, it is becoming less acceptable as control criteria become more stringent.

Process improvements and modifications. In-plant improvements can reduce or completely eliminate the generation of process wastewaters. This approach can result in improved process yield and by-product recovery and reduced overall treatment costs. However, the intended process modifications must be individually and carefully evaluated prior to their implementation, as reduction or elimination of a pollutant may create a different problem. A typical example is the use of air pollution scrubbers, which create

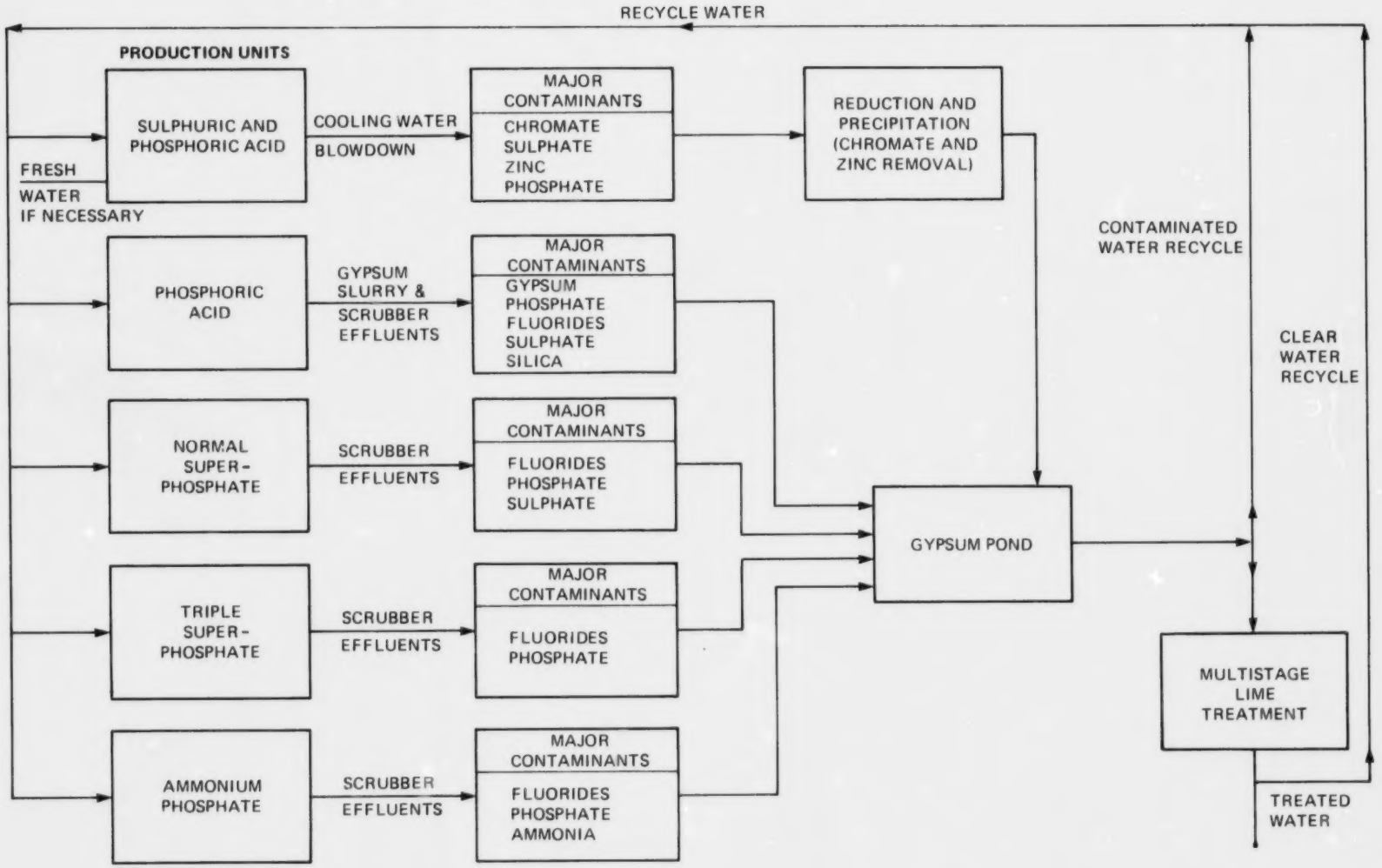


FIGURE 19 SUMMARY OF PHOSPHATE FERTILIZER COMPLEX EFFLUENT TREATMENT PROCESSES

their own wastes. A significant controlling factor in the evaluation of these modifications is existing control requirements set by various regulatory agencies.

In the manufacture of triple superphosphate, the use of concentrated (68 to 75%) phosphoric acid would effectively minimize the generation of aqueous effluents. This is achieved by eliminating the need for a dryer, which results in less off-gases scrubber water usage (26).

Recycle and reuse. Recycling and reusing wastewater can be a most effective and inexpensive method of controlling industrial waste loads. It is widely practiced in the phosphate fertilizer industry. Effective reuse of water reduces the volume of wastewater to be treated and also reduces the need for large volumes of fresh water. The phosphate fertilizer industry recycles more than 90% of its gross water requirements. In wet process phosphoric acid plants and phosphate fertilizer complexes, process effluents, spillages, and cooling water blowdown (after chromate removal) are all discharged into the gypsum pond. This gypsum pond water serves as a recycle reservoir for the contaminated water. Because this water is contaminated, it cannot be used for all plant process needs.

A large quantity of wastewater in the phosphate fertilizer industry originates from air pollution scrubbers. Several techniques have been developed for recycling this scrubber water and recovering the fluoride content, as fluosilicic acid. In the industry, it is now standard practice to recycle scrubber water to recover a 20 to 25% solution of hydrofluosilicic acid as a by-product. Considerable research is currently under way to extend the uses for this by-product. Not all fluorides in the gas streams can be removed using a recycled scrubber solution. If greater than 95% fluoride removal is required, as indicated in present trends of air pollution regulations, a second-stage scrubber must be employed where the gas is scrubbed with fresh water and usually with no recycling.

Physicochemical treatment. The availability of gypsum ponds in a phosphate fertilizer operation greatly reduces the volume of wastewater discharge to the environment. Streams from scrubbing operations, cooling towers, and operational spills/leaks are all discharged into this collection pond, so the overflow is normally the only discharge. The amount of this overflow is dependent upon pond evaporation, the amount of rainfall, and subsurface water seepage.

The wastewater in a gypsum pond contains substantial quantities of various contaminants, such as fluoride, phosphate, etc., and any excess pond water must be treated, usually by lime neutralization followed by settling. The treated water is then

discharged or recycled back to the plant. In most cases, multistage liming is required to obtain the desired level of impurity removal. Various methods are described below.

Multistage liming. Lime neutralization and subsequent settling is a proven and effective method of removing phosphates and fluorides from wastewaters. To date, this is the only feasible approach to reduce these pollutants to less than 20 mg/L. This technology was developed within the municipal treatment field where chemical precipitation has been employed for the removal of phosphate and is well documented in the literature (27,28,29,30).

Multistage liming consists of selective precipitation of the fluorides and phosphates by pH control to effectively remove these materials from the wastewaters. The typical process is shown in Figure 20. Because the pH of gypsum pond water varies between 1 and 3, lime is initially added to increase it to 3.5 to 5.0. Retention time for precipitation is 10 to 15 minutes and the resultant slurry is sent to a mechanical thickener to settle out fluoride ions, as calcium fluoride. This sludge is normally discharged to the pond.

This process reduces the fluoride content of the effluent to 40 to 60 mg/L and 5 to 10% of the phosphate is also removed. The thickener overflow then goes to a second reaction tank to raise the pH to 6 to 7 with further lime addition. Additional phosphates precipitate out, as calcium phosphate, to give a final effluent containing 15 to 20 mg/L fluorides (F) and 10 to 30 mg/L phosphates (P_2O_5).

The treated pond water may also contain 20 to 60 mg/L ammonia-nitrogen, which may have to be treated further prior to discharge depending on water pollution control requirements. The final effluent, alternatively, can be recycled to the plant.

If an on-site gypsum pond is not available and fluoride recovery is not practical, lime neutralization can be used for fluoride removal from scrubber effluents. For 99% fluoride removal, a two-stage scrubbing unit is needed. The wastewater from the second scrubber is treated with lime before recycling. A typical flow diagram of this process is shown in Figure 21.

Legal (31) has patented an improved liming process that relies on specific pH control to recover fluorides and phosphates as by-products. First-stage precipitation removes 28 to 30% of the fluoride as its calcium salt; in the second stage, 35 to 40% of the phosphates are removed. The advantage of this process is that the effluent contains only low levels of fluoride and phosphate. pH 7.0, these levels would be less than 10 mg/L, whereas at pH 8.5, the phosphate discharge would be between 30 and 80 mg/L.

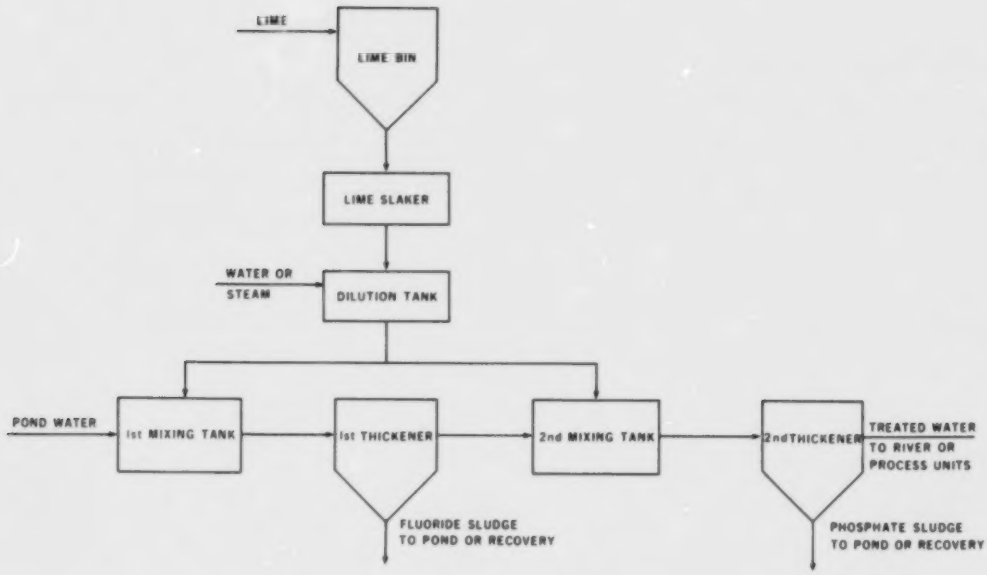


FIGURE 20 FLUORIDE AND PHOSPHATE REMOVAL - MULTISTAGE LIMING TREATMENT

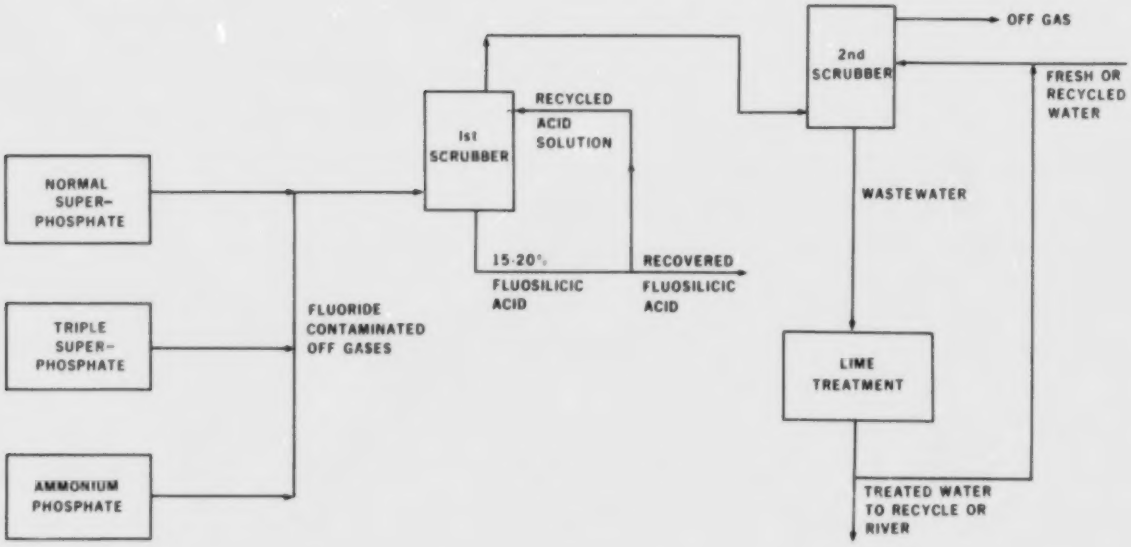


FIGURE 21 SCRUBBING AND LIME TREATMENT PROCESS FOR PHOSPHATE FERTILIZER PLANTS WITHOUT GYPSUM PONDS

A two-stage lime slurry precipitation process in a Florida phosphate fertilizer plant reduces the fluoride and phosphate levels in the effluent to less than 5 mg/L from a high concentration of 1700 mg/L and 5000 mg/L, respectively, in the influent (32). Thus, careful operation of a lime neutralization process, with positive pH control, can ensure less than 10 mg/L discharge of fluoride and phosphate.

The treatment of gypsum pond water with lime for pH, fluoride, and phosphorus control also results in the removal of radionuclides. Tests at plants showed that treatment with lime is highly efficient in removing over 94% ^{226}Ra, 96% uranium, and 99% ^{230}Th from the process water.

This large reduction is attributed to the amount of available sulphate ions in the gypsum pond water enabling large-scale coprecipitation of calcium-radium sulphate, the relative insolubility of radium sulphate, and the probable precipitation of uranium and thorium along with $CaSO_4$ and other components.

Granulated slag treatment. The Tennessee Valley Authority has developed a novel treatment scheme (33) for fluoride removal from scrubber water prior to its discharge. The waste is treated with granulated slag, which is an alkaline mixture of calcium silicate and aluminum silicate. This solid waste material is capable of removing 95% of the fluoride from the wastewater and also the majority of the phosphate. The recovered fluorides can be used in the manufacture of cryolite and aluminum fluoride. In the actual operation, the scrubber water percolates through a slag bed in an open pond and reduces the wastewater fluoride level from 700 mg/L to 25 to 30 mg/L.

Chromate removal. Chromate compounds must be removed from cooling tower blowdown prior to discharge to a gypsum pond or a receiving stream. Their removal is achieved by the reduction-precipitation method as described earlier for chromate removal in the nitrogen fertilizer industry.

Miscellaneous methods. In the municipal wastewater field, several other phosphate treatment schemes are being developed because chemical treatment is expensive and tends to create its own water pollution problems. Ion exchange was indicated as a viable treatment method, but has yet to be proven in large-scale plants. The inherent problems encountered in this method are fouling of resin beds and the difficulty of regeneration. Phosphate can be precipitated from wastewater without the aid of chemicals by altering the pH and relying on the existing ion content of the solution (5). However, this process may not be feasible for the treatment of phosphate fertilizer wastewaters.

Phosphates in municipal wastewaters can be removed by adsorption onto acid-treated alumina or fly ash. However, application of the method to this industry is doubtful (34) as more than 95% pollutant removal is not achievable.

Other treatment processes for phosphate removal from municipal wastewaters include magnetic filtration (35), foam fractionation (36), and coagulation and filtration (36). The effectiveness of these processes, however, has yet to be demonstrated for the phosphate fertilizer industry.

7.2.2 Water Pollution Control Measures. Existing effluent treatment methods and major contaminants discharged to water bodies from phosphate fertilizer plants in Canada are summarized in Table 15 and Table 8 respectively.

In-plant control measures. In-plant improvements can be employed to reduce or completely eliminate the generation of process wastewaters. These process modifications vary from plant to plant. A total recycling approach is taken by five of the nine plants operating in Canada.

As indicated earlier, a significant quantity of wastewater in the phosphate fertilizer industry originates from air pollution scrubbers. Several techniques have been developed for recycling this scrubber effluent and recovering the fluoride content as hydrofluosilicic acid and fluoride. Information related to in-plant control measures is compiled in Appendix Table B5.

Most phosphate fertilizer plants have taken steps to reduce wastewater discharges and contaminant loadings. The following summary includes some of the techniques used by plants in Canada.

1) The water system in most plants is a closed-loop system and no contaminated water is discharged. Potential water pollution problems do exist if there is sufficient rainfall to cause the gypsum pond to overflow, and from pond seepage.
2) Sulphuric acid plant cooling coils are prone to accidental breaks, which will result in the cooling water quickly becoming contaminated. Most plants have installed a reliable, continuous pH and/or conductivity monitoring system to detect such leaks so that immediate action can be taken.
3) Any phosphate complex containing an ammonium phosphate unit will have NH_3-N in the contaminated water system. Lime treatment will not reduce the N content, although at high pH ammonia loss to ambient air can occur. Ammonia enters the

TABLE 15 WATER POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS

Plant	Phosphoric Acid Process Effluent	Phosphoric Acid Plant Cooling Water	Gypsum Pond Seepages
CIL, Courtright	Scrubber effluent, spills, wash-down, plus all other process effluents, are sent to the gypsum pond. Recycled gypsum pond water is used in scrubbers for washdown, etc. Hydrofluosilicic acid is recovered as a by-product.	All cooling water is once through and is returned to the St. Clair River. The cooling water is noncontact and is thus not contaminated.	All seepages are collected and pumped back into the pond.
Simplot Chemical, Brandon	Phosphoric acid is purchased.	NA	NA
Cominco, Trail	Fluoride levels in effluents are reduced through the production of H_2SiF_6, an acid used in the electrolytic refining of lead and also for fluoridation purposes. The Utah rock causes some foaming in the digesters and vacuum cooler, with minor carryover of acid to the condenser water. A high degree of extraction of acid from the filter cake is achieved.	All cooling water is twice through and is returned to the river.	The gypsum is discharged to a river.
Western Co-op, Medicine Hat (Not producing phosphate fertilizers at present)	All water required for scrubbers, barometric condensers, etc. is recycled and returned to the gypsum pond. Spills, wash water, etc. also go to the gypsum pond.	Cooling water is recycled to the gypsum pond.	There is some seepage from the pond; however, springs in the area are sampled to check levels of contamination. Water from the gypsum pond is used for irrigation purposes during the summer.
Cominco, Kimberley	Rock plant floor drain and impinger effluent go to a clarification pond. The clear water goes to the sewer. Gypsum pond water and cooling pond water are recycled. Scrubber effluent is recycled. Fresh water for vacuum pumps is returned to the river.	Cooling water is recycled to the cooling pond. There is no blow-down required.	Seepage from the gypsum pond that is not picked up and returned to the pond flows into a creek.

Ammonium Phosphate Process Effluent	Storm Runoff	Sanitary Effluent	Sulphuric Acid Plant Wastewaters
Dust scrubber effluent plus spills, washdown, and all other process effluents are sent to the gypsum pond.	Runoff effluent is collected and sent to the gypsum pond.	All sanitary effluent from the entire plant goes to a total oxidation sewage disposal system.	Acid purchased.
Fumes and dust from the neutralizer pass through a liquid scrubber. The liquid is recycled to the neutralizer. There is essentially no liquid effluent. Any effluent created is used for irrigation during the summer and goes to a holding pond during the winter.	Storm water is separated and goes to the river or to the irrigation pond during the summer.	Sanitary effluent goes to the city sewage treatment plant.	Acid purchased.
Thickeners clarify evaporated phosphoric acid. The underflow slurries of settled solids plus acid are used as feed for the 16-20-0 process or returned to the acid digester. Wastewater used to remove scale from equipment goes to the sewer. Scrubber effluents from the phosphoric acid and ammonium phosphate plants are recovered. Final clean-up water goes to the sewer.	Storm runoff is combined with other plant effluents.	Sanitary effluent goes to the sewer.	Sulphuric acid production is part of the pollution control of the metallurgical complex where more than 95% of the sulphur is reclaimed.
Any process spills, leaks, etc. go to a sump. This water is recycled to the phosphoric acid plant to wash the phosphoric acid filter.	Under normal conditions, there is no runoff. Provisions have been made to hold any runoff in a pond. Some runoff also enters the gypsum pond.	Sanitary effluent from the septic tanks goes to the gypsum pond.	Liquid effluent from this plant consists mostly of cooling tower and boiler blowdown. These wastewaters go to a settling basin.
All scrubber effluents are recycled to process. Process spills and wash water are recycled.	Half the storm runoff is recycled and half goes to the river.	Sanitary sewage goes to the city sewage treatment plant. A small amount goes to septic tanks.	The acid plant coolers are once-through cooling; thus, there is no blowdown. Floor drains and spray-trap drains go to a pond.

TABLE 15 WATER POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS (Cont'd)

Plant	Phosphoric Acid Process Effluent	Phosphoric Acid Plant Cooling Water	Gypsum Pond Seepages
Belledune Fertilizer	All pollution control scrubbers use seawater, which is discharged to Chaleur Bay. The gypsum slurry, barometric condenser wastewater, spills, wash water plus all other wastewaters go to Chaleur Bay. Close control is maintained to ensure that only traces of acid remain in the gypsum cake.	Cooling water is once through and is discharged to Chaleur Bay.	NA
Esso Chemical, Redwater	All contaminated effluent from the plant is recycled to the gypsum pond or cooling pond. Evaporation loss exceeds input. Clean water is discharged to the river via a settling pond.	Cooling water is recycled to the cooling ponds.	Water seeping through the dykes is contained by the outer perimeter clay dykes and drains back to the cooling pond. Monitoring wells are placed around the pond to check for seepage to groundwater.
Sherritt Gordon, Fort Saskatchewan	All condensates, scrubber liquids, and wastewaters are discharged with the gypsum to one of three ponds. Clear overflow from the gypsum pond is collected in the cooling pond from which it is recycled to the plant.	Cooling water is recycled to the cold well.	Water seeping through the dykes is collected in ditches and returned to the ponds.
Western Co-op, Calgary	All contaminated effluent from this plant is recycled to the gypsum pond. Any clean water is discharged to the sewer and goes to the river via a retention pond.	Cooling water is recycled to towers. The blowdown is discharged to the river via a retention pond.	Seepage from the dykes is collected in ditches and recycled to the ponds.
International Minerals and Chemical Corporation Ltd.	This plant is closed at present.		

Ammonium Phosphate Process Effluent	Storm Runoff	Sanitary Effluent	Sulphuric Acid Plant Wastewaters
All spills and floor washings go to a sump. The effluent is pumped to the phosphoric acid plant to wash the acid filter.	Storm runoff is collected in ditches and flows to Chaleur Bay.	Sanitary effluent goes to a primary treatment plant. The effluent from the primary treatment plant goes to Chaleur Bay.	There is no sulphuric acid plant. Miscellaneous Studies have been conducted to recover steam condensate to reduce boiler feed-water usage. Boiler blowdown goes to the sewer.
Any process effluent not recycled in the plant is recycled to the cooling pond.	Storm runoff is separated and can flow to the river, either directly or via the settling pond. It can also be contained in a holding pond and directed to the gypsum ponds.	Sanitary effluent goes to the injection well, to the river, or may go off-site to a lagoon.	The liquid effluent from this plant consists almost entirely of cooling tower and boiler blowdown. Boiler blowdown and miscellaneous effluents go to the river. Cooling tower blowdown goes to the settling pond.
Scrubber liquor is reused in the process. Any leaks, spills, etc. that are not recycled are sent to the gypsum pond.	Storm runoff is collected in ditches and flows to a collection pond. Pond overflow goes to the river.	Sanitary effluent, after septic treatment, is combined with some other plant effluents and flows to a river.	Blowdown from the cooling towers and boilers and the backwash from the demineralizers, which is the only wastewater from this plant, are discharged to the river.
Any process effluent not recycled to processes is sent to the gypsum pond.	Storm runoff is collected in a holding pond, which is continuously returned to the gypsum ponds. Overflow leaves the property and may eventually reach the river.	Sanitary effluent from septic tanks flows to a river via a retention pond.	Liquid effluent from this plant consists of cooling tower and boiler blowdown, which are discharged to the river.

contaminated water principally through the ammonium phosphate plant gas scrubber system and from washdown and spillage. Plants that might have excess gypsum pond water segregate these process streams and either introduce the ammonia-bearing wastewater back into the process or treat it for ammonia removal. Plants that have no excess pond water do not worry about ammonia entering the pond water system.

4) In the production of phosphoric acid, the H_2SO_4 must be diluted before being used. Fresh water for this dilution step represents about 50% of the total fresh-water intake of a phosphoric acid plant. Some plants use clarified pond water for this dilution step, which helps to create a negative water balance.

5) Fluoride emissions from phosphate fertilizer plants are controlled by scrubbers using gypsum pond water or cooling pond water as the scrubbing medium. Spent scrubbing water is returned to the pond system without chemical treatment.

6) A few alterations have been introduced to the scrubbing system design to recover fluorides as marketable, 23% fluosilicic acid by-product.

External control measures. The availability of gypsum ponds in a phosphate fertilizer operation greatly reduces wastewater discharges to the environment. Streams from scrubbing operations, such as liquid from barometric condensers that treat gases from the reactor, vacuum cooler, and vacuum evaporators that concentrate the wet process phosphoric acid; liquid from scrubbers that treat gases from the acidulation reactor, filters, hot wells, and filtrate tanks; liquid from scrubbers that treat gases from the ammonium phosphate reactor, granulator, dryer, and cooler; and liquid from scrubbers that treat gases from the reactor, den, and storage area in the production of normal superphosphate and triple superphosphate, and gypsum slurry, etc. and spills and leaks are all discharged into the gypsum pond so that normally no discharge is required.

These storage areas are surrounded by dykes with earthen bases and gypsum piled on top. These earth/gypsum dykes tend to have continual seepage of highly contaminated water; however, it is normal practice to have seepage collection ditches all around the perimeter of the dyked area. The seepage is collected and reimpounded, thus preventing contaminated wastewater from reaching natural drainage streams.

Other wastewater streams, such as septic tank overflow, once-through cooling water, some storm water runoff, cooling tower blowdown, boiler blowdown, and raw water treatment effluent, are monitored on a continuous basis. Some plants have retention ponds where any solids settle out and equalization takes place. Other plants add caustic (e.g., NaOH) or acid for pH control.

7.3 Screening and Verification Program

7.3.1 Purpose and Method. As part of a new environmental approach for the 1980s, the Department of the Environment has developed a toxic chemicals management program. The first task of this program is to identify those industries that discharge toxic substances.

A previous study (St. Clair River study) involving only one fertilizer plant revealed some toxic substances in the effluent from the fertilizer complex; however, these toxic substances appeared in the intake water in the same concentration ranges. To be absolutely certain, a screening survey was undertaken in the present study at five fertilizer plants representing the entire cross section of the industry. The main purpose was to identify and characterize conventional parameters, toxic substances, and health effects. The information gathered from the survey would be used to determine the priorities of the industrial sectors for more in-depth surveys. Composite samples were collected from 24 locations. From each plant, three samples of final effluent, one sample of intake water, and one sample from another location, as suggested by personnel at individual plants, were taken. At one plant, only two samples of final effluent were collected. All samples were 24 hour composite samples. The samples were analyzed for conventional parameters, such as pH, suspended solids, and nitrogen; toxic substances/priority pollutants, as indicated on the U.S. Environmental Protection Agency list of 129 priority pollutants; health effects, such as mutagenicity/carcinogenicity (Ames test) (only one final effluent sample from each plant was tested); and acute toxicity. In addition, special grab samples were collected for the analysis of volatile priority organics.

Thirty-two samples (from five sites) were shipped to the Wastewater Technology Centre (WTC) in Burlington. The analyses of organic compounds and metals for all samples were carried out at WTC. The conventional parameters for samples from the Ontario region were also analyzed at WTC. Environment Canada regional laboratories analyzed the samples from plants in their respective regions for conventional parameters and some metals. Some samples of final and intake water were analyzed for fluoride by Bondar-Clegg and Company Ltd., Ottawa. Nine samples were tested for monoethylamine by Environment Canada Ontario Regional Laboratory, Ottawa. One separate 23 L, 24 hour composite sample of final effluent was collected from each plant and shipped to the British Columbia Cancer Research Centre in Vancouver for mutagenicity/carcinogenicity tests. All sample bottles were cleaned, prepared, and supplied by WTC and Environment Canada regional laboratories. In most cases, the samplers normally used by

the plants were used, after changing the tubing. In some locations, however, the samplers used were provided by Environment Canada laboratories.

7.3.2 Methodology. The sampling and analytical procedures outlined in *Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations*, published in the U.S. Federal Register, December 3, 1979, were followed in the Environment Canada regional laboratories and the British Columbia Cancer Research Centre. The samples were collected in the appropriate containers and stored at 4°C prior to and during shipment. Upon arrival at the laboratories, the test samples were stored at 4°C until analyzed.

7.3.3 Results.

Conventional pollutants. All of the results obtained from the screening surveys carried out in 1980/81 are tabulated in Appendix Table C1. Contaminant levels in the final effluent from all fertilizer plants are also tabulated in Tables 4 and 8 (1984/85 data). Some of the pollutant concentration levels might be lower in the 1984/85 data, which is indicative of the additional control measures installed.

The nitrogen content in the final effluent from one plant is very high. The control program being undertaken there is expected to reduce the nitrogen level significantly, which will enable the plant to meet the provincial agency requirements. Suspended solids, phosphate, and chemical oxygen demand levels in the final effluent from nitrogen fertilizer plants are all fairly low and the pH of the final effluent is within the recommended range of 6 to 9.

Two phosphate fertilizer plants, however, discharge the gypsum slurry from the wet process phosphoric acid plant to the sewer, which lowers the pH to a very low range of 2 to 3. The suspended solids, sulphate, phosphate, and fluoride levels in the final effluent from these two plants are also very high.

Priority pollutants.

Metals. As shown in Tables 11 and 12 and Appendix Table C2, all metal concentrations are very low, except for chromium. In fact, most metal concentrations in the final effluent are only slightly above the levels in the intake water. The higher chromium levels are likely due to the discharge of untreated cooling tower blowdown from some of the plants. The technology for the removal of chromium from wastewaters is available and should be utilized. The concentrations of the other metals, however, are too low to be treatable by conventional techniques, e.g., chemical precipitation.

Organic pollutants. As noted in Appendix Tables C3 and C4 to C7, the concentrations of priority organic pollutants found in the final effluent of fertilizer plants are very low. Comparing these values with the ambient water quality criteria tabulated in Table 13 for acute and chronic toxicity, one would not likely classify these effluents as being hazardous to aquatic life (as far as organic pollutants are concerned), even taking into account the possibility of antagonistic or synergistic effects. Detection limit and quantitation limit are different; hence, a trace was reported when the compounds could be identified but were not present in sufficient quantities to be reported (generally less than 1 µg/L). A range (1 to 10 µg/L) is reported for the detection limit.

The following pairs of compounds co-elute and cannot be distinguished by mass spectrometry: benzo(b) fluoranthene and benzo(k) fluoranthene; anthracene and phenanthrene; chrysene and benzo(a) anthracene; and 1,3- and 1,4-dichlorobenzene.

The following compounds are difficult to quantitate, resulting in possible inaccurate results: isophorone, 1,2-diphenyl hydrazine, N-nitroso-di-n-propyl amine, hexachlorocyclopentadiene, N-nitroso-dimethyl amine, and nitrophenols. Some samples formed emulsions, which created problems during extractions.

Biological testing. During the screening program, final effluent samples from some of the fertilizer plants were collected to measure the acute toxicity of effluents with respect to aquatic organisms. In addition, provincial environmental agencies and Environment Canada regional personnel have collected samples over the past 2 or 3 yr from most of the plants for acute toxicity testing. The results are tabulated below.

Plant	Result
Canadian Fertilizer, Medicine Hat	Not acutely lethal
Western Co-op, Calgary	35%<LC_{50}<65%
Western Co-op, Medicine Hat (no final effluent, only gypsum pond seepages)	NA
Cominco, Calgary	Not acutely lethal
Cominco, Carseland	Not acutely lethal
Cominco, Kimberley	NA
Cominco, Trail	Acutely lethal
Esso Chemical, Redwater	Not acutely lethal
Sherritt Gordon	10%<LC_{50}<35%
Simplot Chemical	20% <LC_{50}<40%
CIL, Courtright	Not acutely lethal
Cyanamid of Canada	Not acutely lethal
Nitrochem	1%<LC_{50}<28%
Belledune Fertilizer	Acutely lethal

The acute toxicity test results indicate that the final effluent from some fertilizer plants (from the entire complex) is nonlethal. At other plants, 100% effluent was toxic; thus, the samples had to be diluted with diluent water to determine the effluent concentration, expressed as a percent volume, that is lethal to 50% of the test organisms within 96 hours. For all or most tests, the test organism used was rainbow trout. When mortality is the effect measured, the toxicity is expressed as the median lethal concentration (LC_{50}). If plants had an LC_{50} of less than 100%, it was normally a result of too high a nitrogen content (particularly un-ionized ammonia), too high a fluoride content, or the pH not being in the 6 to 9 range.

In addition, five final effluent samples from fertilizer plants were tested for genotoxic activity using a battery of four short-term bioassays. Each straight effluent was tested for mutagenicity in *Salmonella typhimurium* using a suspension test procedure. The concentrated extracts, prepared from the five effluent samples, were tested for their capacity to induce mutations in *Salmonella typhimurium*, chromosome aberrations in Chinese hamster ovary cells, and DNA damage and inhibit DNA repair in cultured human fibroblasts. The results of this study are summarized in Tables 16 and 17.

No mutagenic activity was demonstrable with any of the five straight effluents in the *Salmonella* mutagenicity test over the dose range tested. (See glossary for explanation of terms.) Four extracts exhibited mutagenic activity, showing a dose-related increase in mutant colony count just reaching the twofold increase above the background selected as one of the criteria for a positive mutagenic response. The mutagenicity was demonstrable primarily in the strains TA100 and TA98. Strain TA1535 was the least responsive.

Two effluent extracts exhibited chromosome-damaging activity in the absence of an *in vitro* metabolic activation mixture (S9) and when S9 was present. In general, the activity was demonstrable over a very narrow dose range.

No DNA repair induction, detectable as unscheduled DNA synthesis, was demonstrable in any of the five extracts. However, one extract exhibited DNA repair inhibition induced by ultraviolet irradiation.

The test results from the different *in vitro* assays were indicative of the presence of genotoxic materials in four of the five effluent extracts. The presence of DNA repair inhibitory activity in one effluent in the absence of a positive response in other tests tends to indicate that no genotoxic material is present. Four extracts demonstrated mutagenic activity in *Salmonella* and two extracts showed chromosome-damaging activity. Two extracts were mutagenic to *Salmonella* but did not induce

TABLE 16 SUMMARY OF TESTING OF EFFLUENT SAMPLES

	Straight Effluent		Extract							
	Salmonella Mutagenicity		*Salmonella* Mutagenicity[a]		Chromosome Aberration[b]		DNA Repair[c]		DNA Repair Inhibition[d]	
		+S9		+S9		+S9		+S9		+S9
Belledune Fertilizer	-	-	+	+	+	+	-	-	-	-
Nitrochem	-	-	+	+	+	+	-	-	-	-
Western Co-op	-	-	+	±	-	-	-	-	-	-
Esso Chemical, Redwater	-	-	+	+	-	-	-	-	-	-
Cominco Ltd.	-	-	-	-	-	-	-	-	+	-

[a] *Salmonella* mutagenicity: +, positive: colony count reaching at least twofold increase above background with a dose response
±, dose-related increase in colony count but not reaching twofold above background
-, negative: neither dose-related nor twofold increase in colony count above background

[b] Percentage of metaphases with chromosome aberrations: -, 0 to 4%; +, >10%

[c] Maximum mean grains per nucleus observed: -, 0 to 4

[d] +, inhibition observed; -, inhibition not observed

chromosome aberrations in Chinese hamster ovary cells. One extract did not exhibit genotoxic activity in either test. For detailed results of the genotoxic activity, refer to Appendix Tables E1 to E13 and to an unpublished report prepared by the British Columbia Cancer Research Centre (38).

7.3.4 Discussion. The disposal of vast quantities of wastes generated each year is of great economic and environmental concern. Human beings and the environment are being exposed each year to a large number of chemical substances and mixtures, some of which may present an unreasonable health hazard. Many of these compounds are mutagenic to lower organisms and there are sound biological reasons to conclude that at least some are also mutagenic to humans.

TABLE 17 SUMMARY OF *Salmonella* MUTAGENICITY TEST RESULTS

	Straight Effluent										Extract									
	1535		100		1537		1538		98		1535		100		1537		1538		98	
		+S9		+S9		+S9		+S9		+S9		+S9		+S9		+S9		+S9		+S9
Belledune Fertilizer	-	-	-	-	-	-	-	-	-	-	-	-	+	±	±	±	±	+	±	+
Nitrochem	-	-	-	-	-	-	-	-	-	-	-	-	±	-	+	-	±	-	+	+
Western Co-op	-	-	-	-	-	-	-	-	-	-	-	-	+	±	-	-	-	-	+	±
Esso Chemical, Redwater	-	-	-	-	-	-	-	-	-	-	-	-	±	±	-	-	-	-	+	+
Cominco Ltd.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: +, positive: colony count reaching at least twofold increase above background
±, dose-related increase in colony count but not reaching twofold above background
-, negative: neither dose-related nor twofold increase in colony count above background

The development of suitable waste management methods requires a means of identifying the "hazardous" portion of this waste load. With the identification of hazardous wastes, proper storage, treatment, and disposal methods can be utilized to ensure the public's health and the integrity of the environment.

During the past few years, mutagenic effects have occupied a prominent place in toxicology. Extensive studies have been devoted to the development of sensitive methods for identifying chemicals that induce mutations and short-term *in vitro* tests are now being used to screen many potable waters, industrial wastewaters, and new compounds to identify those that may pose a genetic or carcinogenic hazard to humans.

Identifying genotoxic hazards can be accomplished by epidemiological studies, whole-animal studies, short-term *in vitro* tests, or a combination of the three. Epidemiological studies are potentially the most definitive; however, these studies can be difficult to perform and interpret, i.e., connecting the cause and effect, are costly, and must be conducted after humans are exposed to the hazard. Animal studies are normally the next best approach; however, these studies are slow and expensive and require large amounts of the sample in question. We must also realize that, in the case of substances that have been shown to be carcinogenic in animals, toxicological extrapolation to man in quantitative terms is difficult because, for the majority of environmental carcinogenic chemicals, data on dose/effect relationships, especially at low levels, are very limited. *In vitro* tests for genotoxicity are more rapid and less expensive but also suffer from the need to correlate any results with animal or human effects. Combining *in vitro* tests with whole-animal and human exposure situations could provide important exposure assessment information but would not overcome the extrapolation problems.

Interpreting mutagenicity in environmental samples introduces complications beyond those encountered in screening pure compounds because a clear mutagenic response and a linear dose-response curve, as one generally finds with pure compounds, may not always be seen. Mixtures often have variable or inadequately known chemical compositions. The biological effects of mutagens in complex mixtures are not necessarily additive and there can be synergism and antagonism among mutagens and nonmutagens. The study of complex mixtures requires a combination of the methodology of environmental chemistry and that of genetic toxicology.

Many studies reported in the literature have relied totally on a battery of *in vitro* tests to identify potential chronic toxicity in complex mixtures. Other studies have estimated the hazard associated with pollution by identifying the chemical components of a complex mixture and using this information in combination with models designed to estimate their biological activity.

Studies with animals usually involve exposure to high levels of a single potential carcinogen. However, humans are exposed to a wide range of chemicals that may enhance or inhibit development of the cancer due to low levels of a particular agent. Thus, estimates that a given agent will induce, for example, one tumor in a million persons exposed under these conditions are somewhat speculative. However, exposure to even very small amounts of carcinogenic chemicals is undesirable and poses some risk, and repeated exposure amplifies that risk.

Many of the organic chemicals found in the final effluent from fertilizer plants contain chlorine and bromine. A high percentage of chlorinated and brominated chemicals are mutagens and/or carcinogens in animal cancer tests and, thus, represent a highly suspect class of chemicals, e.g., chloroform, trichloroethylene, tetrachloroethylene, chloromethane, chloropropene, bromodichloromethane, chlorodibromomethane, toluene, and benzene. As shown in Table 13, however, these chemicals were present in very low concentrations and did not exhibit genotoxicity in straight (unconcentrated) effluents, presumably due to the fact that the mutagenic/carcinogenic components were below the limits of detection of the *in vitro* bioassays.

To determine if higher concentrations of the residue organics would elicit a mutagenic response using the four short-term tests, the samples were concentrated 250-fold. As noted in Tables 16 and 17, the extracts demonstrated both mutagenic (in *Salmonella*) and chromosome-damaging activities. Using concentration steps, however, it must be realized that there is a finite chance that (1) compounds of the wastewater may be altered by the procedure chosen; (2) active compounds may be created by concentration of the solutes or their interaction with solvents, other components, or contaminants; or (3) some compounds may be preferentially lost.

To make efficient use of research facilities and limited funds, testing and evaluation of effluents should be based on the principle of stepwise progression. This study, which was at the initial screening level, included obtaining values from the literature on biodegradability, the potential for bioaccumulation, and other aquatic fate processes (see Table 18) as well as testing for aquatic toxicity and performing four short-term *in vitro* tests for mutagenicity. The results of this investigation should be of value to Environment Canada and others in identifying potential hazards and problem areas; monitoring the effectiveness of pollution control mechanisms, containment and recycling practices, and industrial processes; and setting priorities for in-depth and more specialized toxicological studies.

If further investigation is warranted, based on an evaluation by scientists and industrial and other experts from all necessary disciplines, then further monitoring should be carried out. Individual waste streams should be monitored for priority pollutants to determine which streams contain the bulk of the chlorinated hydrocarbons. Some effort should then be made to remove them using one of the treatment methods noted in Table 18. Further monitoring and separating the samples into base, neutral, and acid fractions with genotoxicity testing would indicate how effectively the treatment system is working.

TABLE 18 PRIORITY POLLUTANTS FOUND IN FINAL EFFLUENT FROM FERTILIZER PLANTS AND THEIR AQUATIC FATE AND POSSIBLE TREATMENT METHODS

Parameter	Levels Found in Fertilizer Effluent (µg/L)	Aquatic Fate*	
		Photolysis	Hydrolysis
Chloroform	31-189	Probably not significant	Probably not significant
Trichloroethylene	0-2	Probably does not occur	Probably too slow to be significant
Bromodichloromethane	4-130	No information found	Too slow to be significant fate
Toluene	0-30	Direct photolytic cleavage is energetically improbable	Not significant
Trans-1,2-Dichloropropene	0-9	No data	Appears to be slow, but may be important
Dichloromethane	2-2360	Probably not significant	Probably not a significant fate
Di-n-butylphthalate	0-11	Probably does not undergo direct photolysis	Not considered a competitive process
Bis (2 ethylhexyl) phthalate	0-135	Probably does not undergo direct photolysis	Will hydrolyze slowly, not a competitive process
Phenol	0-20	May be an important degradative process in aerated clear waters	Not significant
Bromoform	0-10	No information	Too slow to be significant
Tetrachloroethylene	0-150	Probably does not occur	Probably occurs too slowly to be significant
Benzene	0-127	Probably not significant	Probably not significant
Chlorodibromomethane	0-2	No information	Too slow to be significant
1,1,2,2-Tetrachloroethane	0-10	Probably not significant in aquatic systems	Appears to occur too slowly to be a significant fate process

Volatilization	Sorption	Bioaccumulation	Treatment**
Primary transport process	Probably not significant	Weak to moderate	Steam stripping and activated carbon adsorption considered best
Primary transport process	Probably not important	Evidence of some accumulation by marine organisms	Gas flotation, activated sludge, granular activated carbon (GAC) adsorption, and reverse osmosis (RO)
No specific information, probably serves as significant transport process	No specific information	May bioaccumulate	Gas flotation with alum and polymer addition or GAC adsorption
Significant process	Cannot be determined	Probably not important	Biological degradation, GAC adsorption, and steam stripping or aeration
Primary transport process	No data	No data, probably not important	Biodegradation
Primary transport process	Probably not significant	Probably does not significantly bioaccumulate	Sedimentation with alum addition or gas flotation with alum addition
Not as important as adsorption	Sorption onto suspended solids and biota probably most important	An important fate process	Gas flotation with chemical addition, sedimentation with chemical addition, and GAC
Not as important as adsorption	Probably most important transport process	An important fate process	Sedimentation with chemical addition, aerated lagoons, and powdered activated carbon
Possibility of some phenol passing into atmosphere	Not significant	Not significant	Sedimentation with alum addition, aerated lagoons, GAC adsorption, or RO
Little information, may serve as significant transport process	No information	Bioaccumulation in organisms may be possible	Powdered activated carbon adsorption
Primary transport process	Probably not important	Evidence of bioaccumulation by marine organisms but not up food chain	Gas flotation with alum and polymer, sedimentation with alum or lime activated sludge
Probably primary transport process	No information, may occur	Likely low bioaccumulation potential	Aerated lagoon, RO, or gas flotation with polymer
Probably serves as a significant transport process	Adsorption onto activated carbon probably significant	May bioaccumulate	Sedimentation with chemical addition
Probably serves as the primary transport process	Data inconclusive	Data inconclusive	Activated sludge, GAC adsorption, sedimentation with chemical addition

TABLE 18 PRIORITY POLLUTANTS FOUND IN FINAL EFFLUENT FROM FERTILIZER PLANTS AND THEIR AQUATIC FATE AND POSSIBLE TREATMENT METHODS (Cont'd)

Parameter	Levels Found in Fertilizer Effluent (µg/L)	Aquatic Fate*	
		Photolysis	Hydrolysis
Acenaphthylene	0-2	Dissolved portion may undergo rapid photolysis	Polycyclic aromatic hydrocarbons (PAHs) do not contain groups amenable to hydrolysis
Pyrene	0-10	Dissolved portion may undergo rapid photolysis	Polycyclic aromatic hydrocarbons do not contain groups amenable to hydrolysis
N-nitrosodimethylamine	0-10	Slow photolysis appears to be the only fate process of any consequence	Probably not important
Butyl Benzylphthalate	0-92	Probably does not undergo direct photolysis in surface waters, indirect photolysis might occur but very slowly	Will hydrolyze slowly under most conditions, not considered a competitive process
Di-n-octylphthalate	0-14	Probably does not undergo direct photolysis in surface waters, indirect photolysis might occur but very slowly	Will hydrolyze slowly under most conditions, not considered a competitive process
2,4-Dinitrophenol	0-1	Slow photolysis may be the main degradative pathway	Slight possibility of hydrolysis if sorbed by clay minerals
Pentachlorophenol	0-4	Occurs under natural conditions, probably important process near the water surface	Not likely an important process
Chlorobenzene	0-6	No data	Probably will not hydrolyze in ambient waters
Trichlorofluoromethane	0-2	Probably not significant in aquatic systems	Too slow to be a significant fate process
Chloromethane	0-468	Probably not significant in aquatic systems	Probably not a significant fate process

* Source: Anon., Water-Related Environmental Fate of 129 Priority Pollutants, U.S. Environmental Protection Agency, EPA-440/4-79-029b (December, 1979).

** Source: Anon., Treatability Manual, Volume I, U.S. Environmental Protection Agency, EPA-600/8-80-042A (July, 1980).

Volatilization	Sorption	Bioaccumulation	Treatment**
Probably not as important as adsorption as a transport process	Adsorption coefficient for PAH and suspended solids high, movement via sediment considered important transport process	A short-term process, readily metabolized	Sedimentation
Probably not as important as adsorption as a transport process	Adsorption coefficient for PAH and suspended solids high, movement via sediment considered important transport process	A short-term process, readily metabolized	GAC adsorption, sedimentation with chemical addition
Probably not important	Probably not important	Probably not important	Aerated lagoons
Not considered as important a transport process as adsorption	Sorption onto suspended solids and biota and complexation with humic substances probably most important transport mechanism	Considered an important fate process	Gas flotation with chemical addition, ozonization, sedimentation with chemical addition
Not considered as important a transport process as adsorption	Sorption onto suspended solids and biota and complexation with humic substances probably most important transport mechanism	Considered an important fate process	Activated sludge, GAC adsorption, sedimentation/filtration
Probably not important	Adsorption on clay minerals should take place	Probably not important	Activated sludge, powdered activated carbon adsorption
Probably does not affect aquatic fate of this pollutant	Sorbed by leaf litter and other organic matter of the watershed	Will bioaccumulate in numerous aquatic organisms	Aerated lagoons, sedimentation with chemical addition, GAC adsorption
Probably volatilizes from water column at relatively rapid rate	Sorption processes may be substantial	Has intermediate potential for bioaccumulation in the lipids of tissue of living organisms	Activated sludge, GAC adsorption
Primary transport process from the aquatic environment	Inconclusive data	Inconclusive data	Gas flotation with chemical addition, polishing lagoons
Primary transport process from the aquatic environment	Probably not significant	Probably does not significantly bioaccumulate in organisms	Filtration, aerated lagoon

8 AIR EMISSIONS CONTROL AND TREATMENT TECHNOLOGY

A considerable effort has been made to eliminate or reduce air emissions from fertilizer plants to an acceptable level. For some areas, this required a significant incremental capital investment above the base plant. In addition, some processes have been modified to reduce emissions and improve utility of raw materials and energy. This section describes the methods and equipment used to control and treat contaminants present in air emissions.

8.1 Nitrogen Fertilizer Industry

This subsection deals with various approaches employed by the nitrogen fertilizer industry for controlling and treating air emissions. The different methods and processes available are briefly described.

8.1.1 Available Technology.

Ammonia plants.

Desulphurization. Steam regeneration of activated carbon beds results in air emissions of carbon monoxide, hydrocarbons, and sulphur dioxide. These emissions are intermittent, ranging from around 8 hours every week to 8 hours every 3 weeks; thus, controls are not normally required. Some plants have installed thermal incinerators to combust the CO and volatile organic carbon (VOC).

The most modern plants in Canada use a hot zinc oxide bed treatment. The ZnO treatment can completely remove the H_2S along with small quantities of carbonyl sulphide, carbon disulphide, and light mercaptans. The bed is replaced about once each year, rather than being regenerated, thus eliminating air emissions.

Primary reformer. There are no pollution control devices used to control emissions from the primary reformer stack. Purge gas is used by many of the plants to supply 15 to 20% of the energy requirements for the radiant heat section of the reformer. Firing the reformer with purge gas can result in increases in NO_x concentrations. In addition, some plants add the overhead gas from the condensate steam stripper into the base of the reformer stack, which also increases the NO_x concentration in the stack outlet. When natural gas is used for firing the furnace and no purge gas or overheads are added, the emissions of NO_x, SO_x, CO, solids, and VOC are low and require no controls. Other uses for the purge gas and overheads are discussed in the following.

Regeneration of the carbon dioxide scrubbing solution. When the potassium carbonate, amine solution, or Sulfinol solution (depending on the system used at the plant) is regenerated by heating with steam, an emission of approximately 98.5% CO_2 is generated. This carbon dioxide stream is used as a feedstock in urea production, is sold to liquid carbonic plants for use in other processes, or is discharged to the atmosphere. If the gas stream is used to produce urea or carbonic acid, the air emissions are eliminated.

Emissions from process condensate treatment. Process condensates containing ammonia, methanol, and carbon dioxide can be steam stripped and the overheads can be treated cryogenically for ammonia recovery or condensed for aqueous ammonia recovery; the methanol is recycled to process. The best available technology, however, includes (1) ammonia removal and recovery using ion exchange techniques, (2) 100% recycling to saturate the natural gas feed to the reformer, (3) concentrating the condensate to produce nitrogen solutions, or (4) utilization of this contaminated wastewater in other areas of the plant, thus eliminating all air emissions.

Purge gas from the ammonia syn loop. Instead of directing the purge gas to the radiant heat section of the primary reformer, boiler house, or nitric acid plant, the hydrogen can be recovered by one of the following methods, thereby increasing the amount of hydrogen available for the production of ammonia.

1) Cryogenic hydrogen recovery (39): The ammonia is first recovered as anhydrous product and water impurities in the purge gas are removed in a pretreatment system to avoid solidification problems within the cryogenic unit. Because of the volatility difference between hydrogen and other components, methane followed by argon and nitrogen are preferentially condensed, leaving a vapour phase enriched in hydrogen. The hydrogen is now available as a product suitable for recycling into the synthesis loop or for other purposes. The tail gas can be handled separately without environmental problems.

2) Pressure swing adsorption unit (40): The natural gas is heated, desulphurized, mixed with steam, and reformed in a reformer. After cooling, the gas goes to a high temperature shift reactor to reduce the CO content. The gas now enters the pressure swing - adsorption stage, which separates it into a pure H_2 stream and a purge stream. The purge stream, however, only contains CO, CO_2, and methane, which can be recycled to the primary reformer. Because no air is introduced into the system, nitrogen must be supplied from an air liquefaction plant.

3) Liquid nitrogen scrubbing: Natural gas is partially oxidized using oxygen from the air liquefaction plant, the CO is converted to CO_2, the carbon dioxide is removed (sent to the urea plant), and the relatively pure hydrogen is scrubbed with liquid nitrogen to remove any argon, carbon monoxide, or methane. Nitrogen carried over from the wash plus additional nitrogen from the liquefaction plant is combined with the hydrogen to produce ammonia. There is no synthesis gas purge. Such a plant exists in Canada.

Nitric acid plants.

Tail gas emissions from the absorption tower. The following methods are available for reducing NO_x emissions from nitric acid plants.

1) Catalytic reduction (41): The tail gas from the absorption tower is preheated by heat exchange with the flue gas. Fuel is added and burned in the catalytic unit to generate heat. The fuel used is normally methane, carbon monoxide, or hydrogen. In the catalytic unit, the fuel reacts with both NO_x and O_2 to form CO_2, H_2O, and N_2. When methane is used, the following reactions take place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$CH_4 + 4NO_2 \rightarrow NO + CO_2 + 2H_2O$$
$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O$$

In the second reaction, or decolorization step, the NO_2 is converted to the colourless NO form; however, there has been no decrease in the total NO_x emitted. With additional methane, however, the NO is reduced to nitrogen. If the reduction is carried out in the presence of high oxygen concentrations (>3%), it must be carried out in two stages to prevent exceeding the upper temperature limit. In practice, 90 to 95% of the nitrogen oxides in the tail gas are decomposed by this process.

2) Extended absorption (42): The most obvious method of reducing NO_x emissions is to increase the absorption efficiency. In the extended absorption process, a second absorption tower is added in series to the existing absorber. Cooling (which can be by refrigeration) is usually required if the inlet NO_x concentration is above 3000 ppm; the gas pressure at the absorber should be at least 730 kPa. The weak acid from the secondary absorber is recycled to the first absorber; thus, there is normally no liquid effluent from extended absorption.

3) Molecular sieves (43): Molecular sieves can selectively absorb NO_x from the absorber tail gas. Removal is accomplished in a fixed bed adsorption/catalyst system, providing recovery and recycling of the NO_x back to the absorption tower.

The absorber tail gas is cooled to around 7°C and then passed through a mist eliminator to remove entrained water and acid mist. The weak acid collected in the mist eliminator is recycled back to the absorption tower. The dried gas now passes through a molecular sieve bed that results in the catalytic conversion of NO to NO_2, which is selectively adsorbed.

Regeneration is accomplished by cycling the adsorbent/catalyst bed after it completes its adsorption step. A portion of the treated tail gas is heated and recycled back through the bed to desorb the adsorbed NO_2. This stream is recycled back to the absorption tower.

4) Wet scrubbing: Wet scrubbing involves treatment of the absorber tail gas with alkali solutions (hydroxides, ammonia, urea, carbonates) to absorb NO and NO_2 as nitrates and/or nitrite salts. If a urea or ammonia solution is used, there should be no water pollution problem as the ammonium nitrate can be recovered.

$$HNO_3 + HNO_2 + (NH_2)_2CO \rightarrow N_2 + CO_2 + NH_4NO_3 + H_2O$$

This process can reduce NO_x emissions from 5000 ppm to 200 ppm.

One version of the wet scrubbing process used in Canada is the "Goodpasture chemical recovery process" (44). This method of abatement employs four stages of absorption and reaction in a liquid/gas scrubber. NO_x removal is achieved through a combination of absorption and reaction. The gas is first scrubbed with acidic ammonium nitrate, generating free nitric acid and ammonium nitrate, and some ammonium nitrite. The gas-liquid mixture exiting the first stage is separated in a cyclone separator. A portion of the ammonium nitrate is withdrawn and sent to the ammonium nitrate neutralizer.

The gas in the second stage contacts cocurrently a second ammoniacal ammonium nitrate solution (pH 8.0 to 8.3) introduced into the second stage. The ammoniacal ammonium nitrate reduces the NO_x content to a level of 200 ppm or less. The gas-liquid mixture exiting the second stage is separated in a cyclone separator. A portion is cycled to the first stage.

The gas now enters the third stage, which involves the venturi scrubber. The venturi scrubber removes any submicron particles of ammonium nitrate or nitrite from the gas stream. The gas and water from the venturi enter the fourth stage, which involves a packed bed. Additional water is added. The gas exiting the fourth stage should contain less than 200 ppm NO_x.

Another version of the wet scrubbing process is the "Masar process" (45). In this process, the tail gas is cooled and scrubbed with chilled water in the first stage. In the second stage, it is scrubbed with a urea solution, which is converted to ammonium nitrate. Final scrubbing of the tail gas is performed with process water. An emission level of 200 ppm NO_x or less is possible.

Ammonium nitrate plants. The selection of a control device depends upon the physical and chemical properties of the particulate, and the characteristics of the exhaust stream containing the particulate. Wet scrubbers are the predominate emission control device used in the ammonium nitrate and urea industries. This is because wet scrubbers are less subject to caking by hydroscopic materials and the scrubbing liquor can be reintroduced into the processes. Because of the importance of wet scrubbers for controlling emissions from this industry, a brief description of certain wet scrubbers is presented, followed by a description of air emission control devices installed in ammonium nitrate plants to control emissions from specific unit processes.

Fume collection hoods (46). The function of collection hoods (Figure 22), used exclusively in prill towers, is to capture emissions by surrounding the spray head and ducting the emissions to a scrubber. About 40 to 90% of the total prill tower emissions are reportedly captured in an airstream representing about 25% of the tower airflow. This reduces the amount of air requiring treatment.

Wetted fibrous filter scrubber (46). The wetted fibrous filter scrubber is often used in conjunction with the collection hood. This scrubber consists of two series of filter elements separated by an atomizing spray chamber. The gas stream first encounters elements of relatively low fibre density, which are irrigated to remove the captured large insoluble particles. The remaining particulates in the gas stream flow into the spray chamber where some of them impinge on the water droplets. The particle laden droplets are then removed from the gas stream by the second set of filter elements (the "high efficiency" elements). These high efficiency elements contain fibres that are compressed

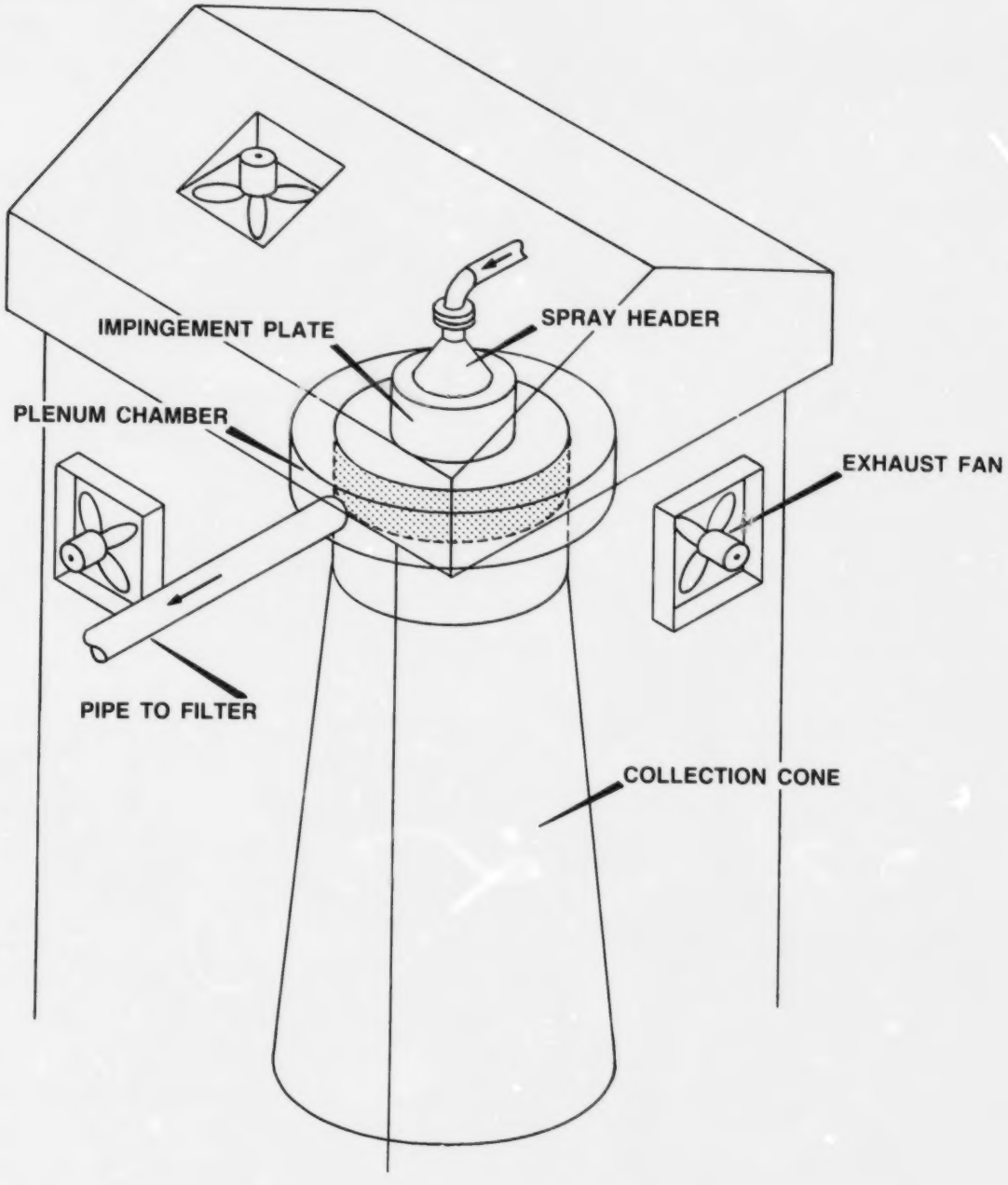


FIGURE 22 PRILL TOWER DUST COLLECTION DUCT

to a greater density than the spray catcher elements. The pressure drop across these elements is about 1 to 5 kPa for this application.

Tray-type scrubbers (7). Particle laden gas enters at the bottom of the vertical tower and bubbles up through perforations or other types of openings in each tray before exiting from the top of the tower (Figure 23). Scrubbing liquor is introduced at the top plate, flows across and over a retaining dam, and reaches the plate below via a downcomer.

Tray scrubbers do not exhibit the same removal efficiency for all particle sizes. The perforations for a well designed scrubber are 2 to 3 μm in diameter. The major factor affecting the efficiency of a tray scrubber is pressure drop; the higher the pressure drop, the higher the removal efficiency. The number of trays, size of the orifices in the tray, velocity of the gas stream passing through the scrubber, and liquid-to-air ratio, which ranges from 670 to 2000 L/1000 m^3, control the pressure drop.

Spray tower scrubbers (7). Spray tower scrubbers consist of vertical or horizontal towers containing banks of spray nozzles (Figure 24). Either cross-flow, countercurrent, or cocurrent spray configurations are used to spray droplets into the gas stream. Particles in the gas stream impinge on the liquid droplets and then are collected and removed from the bottom of the tower. Pressure drops across these scrubbers range from 0.12 to 0.50 kPa, with gas velocities of 0.35 to 1.5 m/s and liquid-to-gas ratios of 400 to 2700 L/1000 m^3.

Factors affecting spray tower performance include droplet size, relative velocity between droplets and gas airflow, and liquid-to-gas ratio. Large droplets provide less total surface area for impaction, thus decreasing removal efficiency. Small droplets, however, which provide a larger total surface area for particle capture, might be entrained in the rising gas stream; thus, an optimum size should be found for each application.

Venturi scrubbers. Scrubbing liquor is injected into the gas stream upstream of the throat area. The gas stream atomizes the liquid into droplets, then accelerates them through the throat. The particles collide with, and are collected by, the liquid droplets in the turbulent area in the throat. The particle laden liquid is then removed from the gas in a cyclonic separator.

Venturi scrubbers normally operate at pressure drops of 2.5 to 20 kPa and liquid-to-gas ratios of 400 to 1300 L/1000 m^3. High gas velocities of 60 to 180 m/s are needed to keep the relative velocities between the gas and scrubber liquid droplets

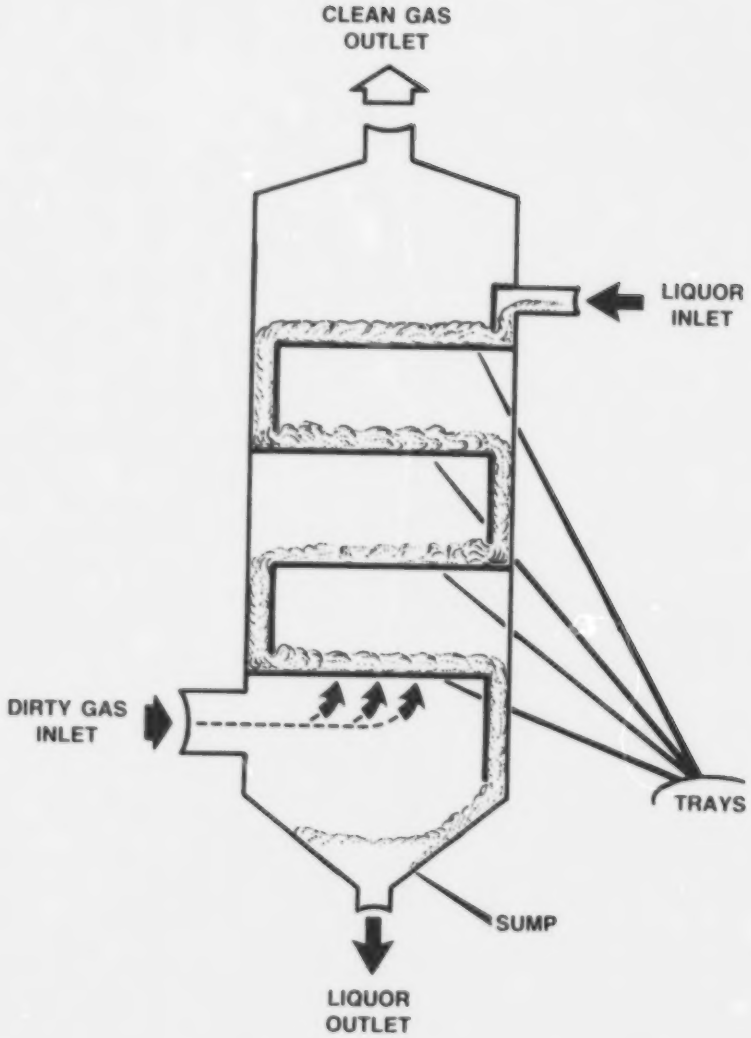


FIGURE 23 TRAY-TYPE SCRUBBER

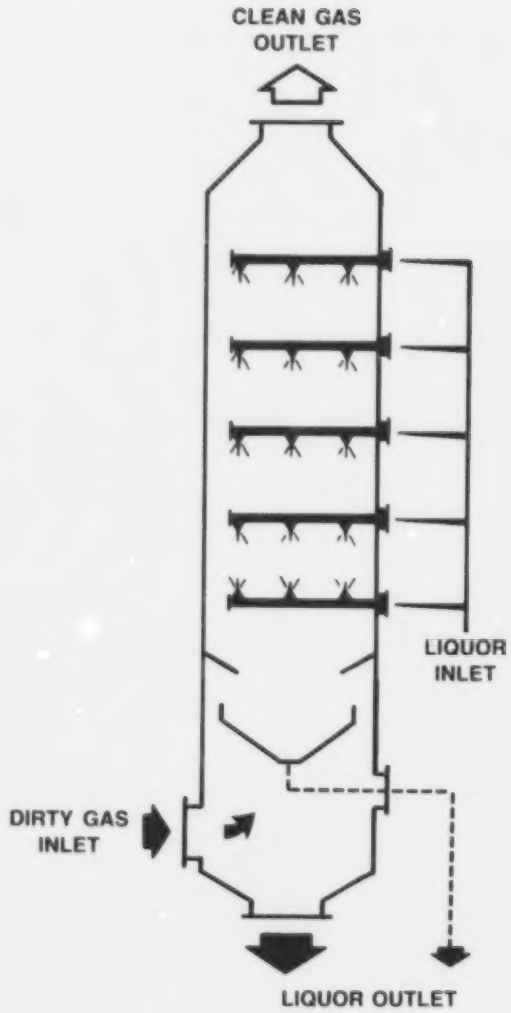


FIGURE 24 SPRAY TOWER SCRUBBER

between 35 and 150 m/s. Operating variables that affect venturi scrubber performance include pressure drop and the liquid-to-gas ratio.

Impingement scrubbers. The impingement scrubber consists of perforated sheets with 0.6 to 3.3 holes/cm^2 and a set of impingement baffles located directly above each hole at a distance corresponding approximately to the position of the vena contracta of the gas jets (Figure 25). The gas enters at the base, where the large particles are removed. The sprays also wash the bottom of the first plate to minimize deposits.

The gas velocity through the jets is 20 to 30 m/s. This atomizes the liquid into droplets on the order of 100 μm in diameter, which act as collecting bodies in the scrubber. The pressure drop is about 0.37 kPa per plate. Higher pressure drops have been developed by using an orifice restriction at the gas inlet or by using a high-velocity slot stage.

Wet cyclone scrubbers (7). Wet cyclone scrubbers impart a rotational motion to the incoming gas by tangentially introducing the gas stream into the scrubber or by directing the gas stream against stationary swirl vanes (Figure 26). Liquid is sprayed through the rotating gas stream either outward from a central manifold or inward from the wall. Particles in the gas stream impact on the liquid droplets. The centrifugal force and the high gas velocity carry the particle laden droplet out to the cyclone wall where a continuous water film washes it down the wall and out of the system. These cyclones generally operate at 0.5 to 1.5 kPa pressure drop, with liquid-to-gas ratios of 270 to 1350 L/1000 m^3.

Neutralizer. The exothermic reaction produces quantities of steam containing ammonia and particulates of ammonium nitrate, but may also contain CO_2 if the off gas from urea plants is fed to the neutralizer. These emissions are controlled by using total condensers, wet scrubbers, and high efficiency mist eliminators. The scrubbing solution is normally recycled to process (to the fines dissolving tank) or is used in liquid fertilizer formation.

Ammonium nitrate emissions from conventional neutralizers without scrubbers range from 1.3 to 1.8 kg/t of product for those plants that do not utilize the urea off gas. On a kilogram per tonne of 100% ammonium nitrate produced basis, nitric acid emissions range from 0.1 to 0.15, and when operating on the basic side, ammonia losses range from 1.5 to 2.5 (47).

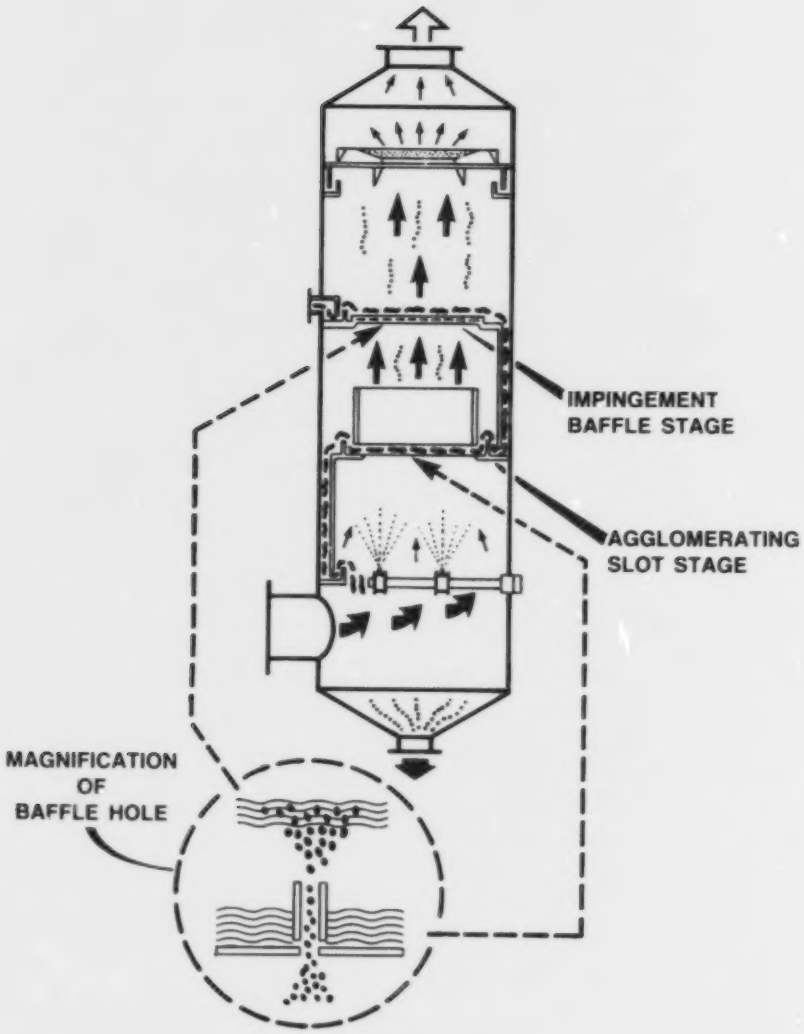


FIGURE 25 IMPINGEMENT SCRUBBER

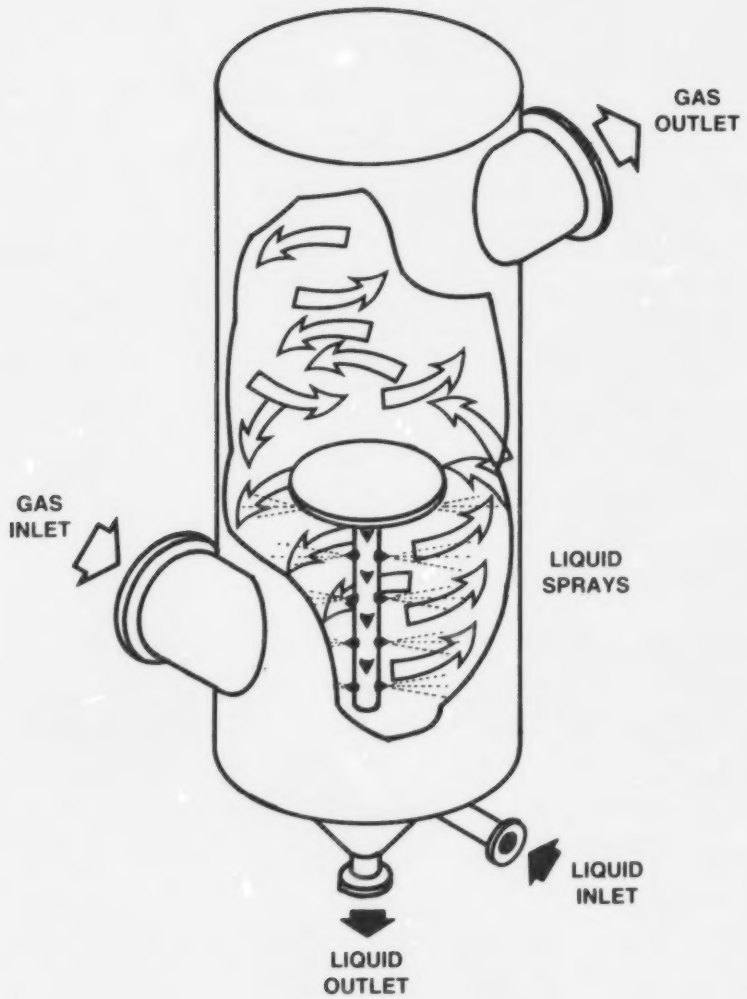


FIGURE 26 WET CYCLONE SCRUBBER

One approach to reducing emission problems has been to redesign the neutralizer to provide greater residence time, more intimate mixing, and lower exit velocity.

If the tail gas is first passed through a packed bed scrubber, where it is in contact with acidic NH_4NO_3 liquor, followed by a high efficiency fibre filter, the total emission, i.e., particulates and ammonia, can be reduced to 70 kg/d or less for a 500 t/d neutralizer (48).

Evaporator/concentrator. Two types of evaporators are used, vacuum and air swept. In the case of a vacuum evaporator, the overhead condensate is contaminated with ammonia and ammonium nitrate. This steam is most conveniently disposed of in the production of liquid fertilizer solutions or as a make-up feed to the nitric acid plant absorber. If barometric condensers with steam ejectors are used, the water is normally recycled to a cooling or gypsum pond. The tail gas leaving an air-swept evaporator contains both particulate matter and ammonia fumes. It generally passes through a venturi scrubber and final cleanup can be incorporated as part of a prilling tower emission control system.

Prill towers. Prills falling through a countercurrent airstream are highly conducive to particle entrainment. In addition, the "fume" resulting from the evaporation, condensation, and solidification of the NH_4NO_3 being prilled is difficult to control.

Dust emissions from a prilling tower can be kept to low levels by using a low air velocity in the tower. When the tower is fully loaded, the carryover of dust must be balanced against the degree of cooling required to solidify the prills. If the tower is only slightly loaded, it will be possible to decrease the air velocity.

The evolution of both ammonia and fume depends upon melt pH, melt temperature, and the air velocity over the surface of the melt. The optimum pH at which the total loss, in terms of nitrogen, is minimized is about 4.5, but there is a tendency to operate at a higher pH to give a less visible plume at the expense of increased ammonia losses. In industrial areas where there are appreciable amounts of sulphur dioxide in the atmosphere, the ammonia may be more serious than is apparent because of the tendency to form ammonium sulphate, which can cause mist formation.

The prilling temperature frequently employed is 180 to 185°C, but it is possible to reduce the temperature slightly below this level, with a resultant reduction in emissions by a factor of about two. The emissions can also be reduced by lowering the air velocity past the surface of the liquid droplets. This can be done by withdrawing some air

at a point below the spray nozzles. Finally, overall emissions are affected by the mechanical design of the top of the tower.

By using carefully designed equipment, taking into account the principles discussed, and accurate process control, it should be possible to reduce the losses due to ammonia and ammonium nitrate fumes to less than 0.05% of production.

Pollution abatement by add-on control, in this particular case, is extremely difficult in view of the large airflow involved as well as the small size of the particles. The first step in the solution to the problem was the development of the Cooperative Farm Chemicals Association shroud (46). The operation of the shroud is based on the fact that the pollutants (microprills, ammonia, and nitric acid fumes) are formed at the prill nozzles. This contaminated air, which represents only a portion of the total airflow, is drawn off and treated. The next step is to treat the airstream collected from the shroud in a set of high efficiency fibre filters, which are irrigated to wash off insolubles as well as the ammonium nitrate. An alternative to this method of abatement is to collect the full airflow from the prill tower and treat it in the same manner.

Prior to utilizing the abatement techniques described above, emissions from a 500 t/d ammonium nitrate prill tower were in the range of 3 t/d. Installation of the Cooperative Farm Chemicals Association shroud and filter system, however, can reduce emissions to 170 kg/d and the opacity to as low as 10% (48).

Predryers, dryers, coolers, and product handling. Cyclones followed by wet scrubbers are the predominate particulate emission control devices used in the ammonium nitrate industry because the scrubbing liquor can be used for solution fertilizers or recycled to process. A variety of scrubber types are used, such as wet cyclone scrubbers, mechanically aided scrubbers, entrainment scrubbers, and tray-type scrubbers.

Urea plants.

Solution formation. Emissions from the solution formation step depend somewhat on whether the method used is the once-through process, partial recycle process, or total recycle process. At many plants in Canada, excess ammonia is condensed and recycled to process. The residual gas streams are sent to the adjacent ammonium nitrate plant as a source of ammonia; thus, there are no emissions from this source. When ammonium nitrate plants are not present, the off gases are recovered by using wash columns, absorbers, compressors, and wet scrubbers.

Solution concentration. Evaporator emissions may be controlled to recover ammonia and urea by using wet scrubbers and demisters and, to a certain extent, condensers (condensers lower the amount of emissions; however, their efficiencies are not as high as those of wet scrubbers). Low energy wet scrubbers can be around 97% efficient; however, because ammonia is removed by absorption into the scrubbing solution, removal efficiencies are strongly pH-dependent.

Emissions from crystallization are less than those from evaporation. Crystallization under vacuum is maintained by a steam ejector on the overhead vent; thus, most of the NH_3, CO_2, and urea will end up in the wastewater. There are only minor emissions to the atmosphere.

Prill towers. Prilling of urea results in emissions similar to those resulting from the prilling of NH_4NO_3; the fumes being difficult to control. Emissions contain ammonia from urea decomposition as well as particulates. One of the most successful emission control scrubbers is the CHEAF scrubber (Figure 27). This system is very efficient in the collection of submicron water soluble particulates and aerosols; thus, it is very suitable for this application (49). Other systems that could be included are the Brinks high velocity or high efficiency mist eliminator, wet electrostatic precipitators (ESPs), and other types of wet scrubbers.

Drum and pan granulators. Emissions from drum and pan granulators are controlled by wet scrubbers. Some of the most commonly used are the Tubulaire, the impingement-type scrubber followed by an evaporative scrubber, and centrifugal scrubbers.

Predryers, dryers, coolers, and product handling. Emissions from these operations are normally low. Wet scrubbers and, in some cases, bag collectors are the only control equipment used for these applications.

Ammonium sulphate plants.

Crystallizers and centrifuge. A vacuum is maintained on the overhead vent by either directly or indirectly cooled condensers; thus, essentially all of the vapour with any carryover of product will end up in the wastewater.

Dryers and screens. Wet scrubbing is commonly used for particulate removal from the dryer and screen vents. The most commonly used scrubbers are the venturi, centrifugal, Rotoclone, packed tower, and spray types. A dry cyclone sometimes precedes the wet scrubber.

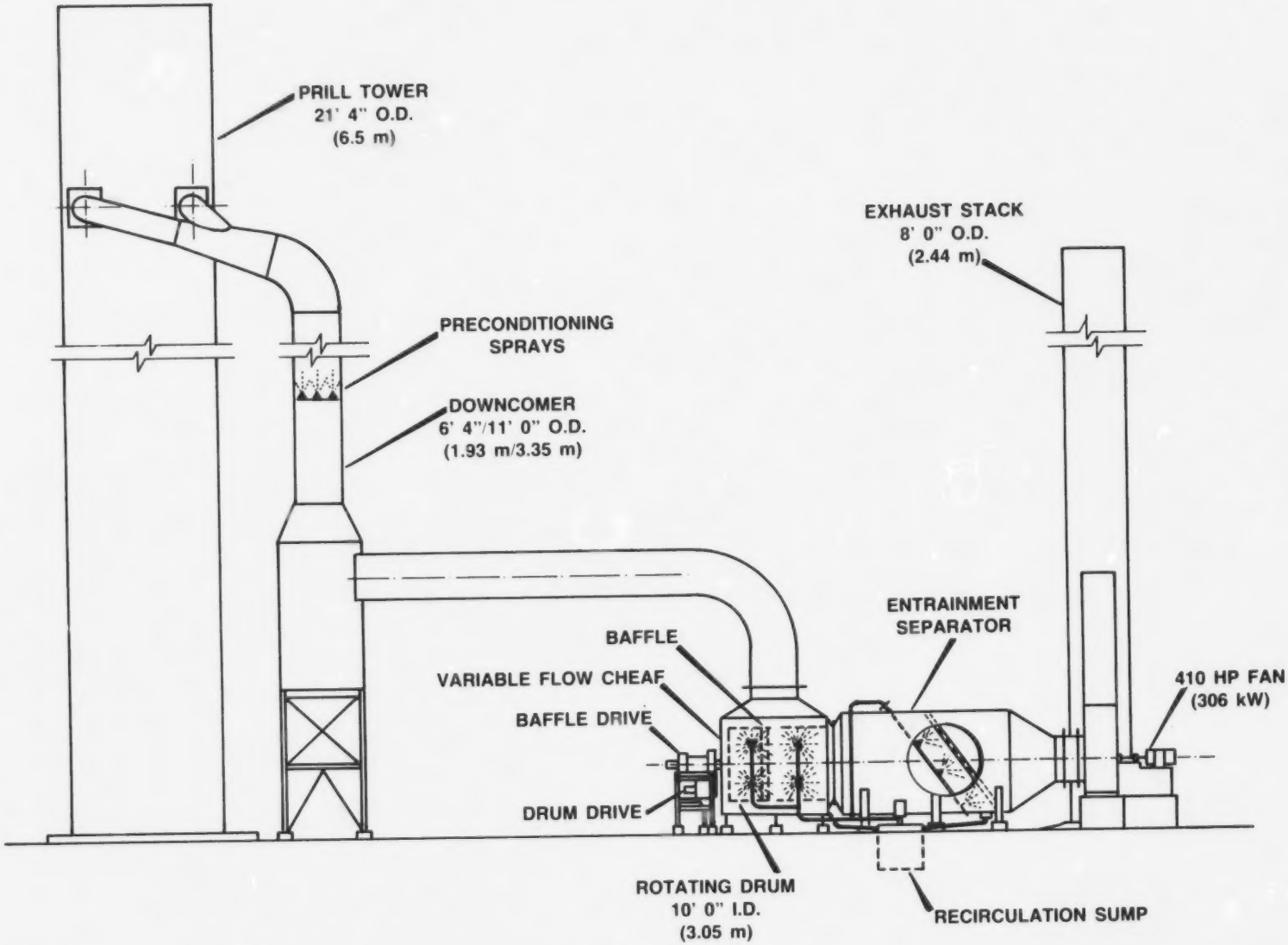


FIGURE 27 "CHEAF" SCRUBBER, ANDERSEN 2000 INC.

Bagging and bulk loading. Dust emissions from the bagging and loading area are normally controlled by cyclones followed by baghouses.

8.1.2 Air Emission Control Measures. This section deals with the various methods used by the Canadian nitrogen fertilizer industry to control air emissions from process and control equipment. Existing control methods are summarized in Table 19. Table 20 shows the major contaminants discharged from nitrogen fertilizer plants in Canada. Most of the data are supplied by industries and, because of differences in sampling procedures, direct comparison between plants should be approached cautiously.

Ammonia plants. Desulphurization units. When the desulphurization units are regenerated, emissions of SO_2, H_2S, hydrocarbons, and CO will be emitted to the atmosphere. These emissions are intermittent and are dependent upon the regeneration cycle. The new Esso Chemical plant uses hot zinc oxide treatment methods; thus, there are no emissions. At least two other plants use a hydrogen slipstream and a cobalt-molybdenum catalyst together with a zinc oxide bed to remove sulphur compounds from natural gas. The zinc reacts with the sulphur to form a zinc sulphide, which is removed every few years and shipped to a catalyst reclaimer.

Primary reformer stack. Emissions of natural gas combustion products (i.e., SO_x, NO_x, CO, and particulates) go to the atmosphere without any controls. Many of the plants do not monitor these emissions. Table 20 summarizes emissions from the plants monitored.

Regeneration of CO_2 scrubbing solutions. As noted in Table 19, seven of the plants that produce urea use part of the CO_2 released during the regeneration of the CO_2 scrubbing solutions for the manufacture of urea. Five plants use some of the CO_2 to produce carbonic acid, dry ice, etc. The remainder of the plants discharge CO_2 to the atmosphere. The estimated amounts of CO_2, ammonia, and hydrocarbons emitted to the atmosphere are presented in Table 20.

Purge gas. The purge gas from the ammonia syn loop is used by the plants in the following ways (the one plant producing ammonia by the partial-oxidation process has no purge gas):

TABLE 19 AIR POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS

Plant	Purge Gas from Synthesis Loop	Carbon Dioxide Regenerator	Tail Gas from Nitric Acid Plant	Neutralizer, Ammonium Nitrate Plant	Reactor Effluent, Urea Plant
Western Co-op Fertilizers, Medicine Hat	The loop purge gas is used as fuel in the radiant heat section of the primary reformer.	By-product carbon dioxide goes to a liquid carbonic acid plant.	A refrigerated absorption tower results in a reduction in volume because the gases involved are more soluble at lower temperatures. The tail gases pass through a demister, heaters, and a Gulf reactor - gives a selective reduction of NO_x on molecular sieve catalyst using NH_3 as fuel.	The exhaust from the Stengel reactor - centrifugal separator passes through a vapour scrubber followed by a total condenser. The stripping air goes to the atmosphere. The scrubber effluent is recycled. The condensate goes to a sump.	NA
Sherritt Gordon, Fort Saskatchewan	The purge gas is used as fuel in the boiler house.	By-product carbon dioxide is vented to the atmosphere.	NA	NA	Ammonia and CO_2 are recovered for process recycling by decomposers, wash columns, condensers, scrubbers, and absorbers. Uncondensed vapours are discharged to the atmosphere.
Simplot Chemical, Brandon	Purge gas from NH_3 synthesis is used as fuel in the radiant heat section of the primary reformer and the nitric acid plant catalytic converter.	By-product carbon dioxide is used to produce urea or goes to a liquid carbonic acid plant for production of dry ice. The remainder is vented.	The tail gas and some natural gas or H_2 purge mixture pass through a catalytic converter containing platinum, which reduces NO_x to N_2, H_2O, and CO_2.	Neutralizer off-gas vapours are partially condensed and the NH_3 is recovered in a wet cyclonic spray scrubber. The remaining CO_2 and water vapour go to the atmosphere. The weak scrubber solution is returned to the process or used in solution.	Off gas composed of NH_3, CO_2, and water vapour (from the off-gas separator) is sent to the ammonium nitrate plant as a source of NH_3 in one plant. The other plant uses absorbers to recover the ammonia.
CIL, Courtright	Purge gas from the Kellogg plant is treated cryogenically to recover ammonia and hydrogen. Residual methane is used as fuel.	The by-product carbon dioxide, which contains CO, NH_3, and hydrocarbon impurities, is used to manufacture urea and is also sold to another company for liquefaction.	The tail gas is heated to the necessary catalyst ignition temperature, mixed with natural gas, and passed into the reactor and over a catalyst bed. Essentially, all of the NO_x is converted to nitrogen.	The exhaust gas from the neutralizer is a jet of superheated steam containing ammonia and droplets of recombined NH_3 and HNO_3 molecules liberated by dissociation. The off gases pass through a demister and Brinks scrubber.	Excess ammonia is removed, condensed, and recycled to the reactor. The gas stream from the carbamate decomposer, which contains ammonia and CO_2, is sent to the ammonium nitrate plant as a reactant feed stream; thus, no gas is emitted to the atmosphere.
Cyanamid of Canada, Niagara Falls	Used as part of the fuel required for the radiant heat section of the primary reformer.	The by-product carbon dioxide is used to manufacture urea, dicyandiamide, and liquid CO_2; the remainder goes to the atmosphere.	The tail gas from the nitric acid plants is treated using the Goodpasture process. The gases are first passed through water, which dissolves some of the nitric oxides; the remaining NO_x subsequently receives an ammonia treatment that destroys both NO and NO_2. An ammonium nitrate solution is recovered.	The exhaust gases are condensed and reused in the plant.	Excess ammonia from the ammonia separator and high pressure decomposer (also some CO_2) is recycled to the reactor via the absorber and condenser. The gas stream from the low pressure decomposer is sent to the ammonium nitrate plant.
Cominco, Carseland	The purged gases from the ammonia syn loop go to the fuel side of the reformer furnace to be burned. Prior to going to the reformer, a portion of the syn converter effluent stream is cooled to -10°C to condense the ammonia. The purge gas with the NH_3 removed is then sent as fuel gas to the reformer.	The by-product carbon dioxide is used in the production of urea. The remainder is vented to the atmosphere.	NA	NA	No effluent.

Concentrator, Ammonium Nitrate Plant	Concentrator, Urea Plant	Prill Tower Vent Gas, Ammonium Nitrate Plant	Prill Tower Vent Gas, Urea Plant	Liquid Storage Tanks, Ammonia Plant
In the Stengel process, a solution of about 98% NH_4NO_3 is produced. The NH_4NO_3 and trace quantities of NH_3 are separated. The NH_4NO_3 is run through an air stripper that reduces the moisture content to approximately 0.3%.	NA	There is no pollution control equipment on the prill tower.	NA	Hortonspheres vent is tied into the ammonia supply to the ammonium phosphate plant.
NA	Urea is crystallized from solution by flashing off water in a flash drum. Flashed vapours are drawn off by steam eductors and pass through water-cooled condensers. Uncondensed vapours are vented to the atmosphere. Vents from the thickener and centrifuges go to the atmosphere.	NA	The crystals are transported to a cyclone collector above the prill tower. The crystals go to a remelter. The exhaust from the cyclone goes to the atmosphere. The exhaust from the prill tower also goes to the atmosphere without air pollution control treatment.	The pressure in the storage tanks is controlled by two refrigeration systems. Ammonia gas is taken from the tanks through liquid catch pots to the suction of the refrigeration compressors. After compression, the gas passes through condensers. The condensed ammonia goes back to storage.
The vent-off from the evaporator contains water vapour and a small amount of ammonium nitrate mist. A demister pad is being tested on the evaporator stack.	The vent from the evaporator, which contains mostly water vapour with small amounts of urea mist, goes to the atmosphere via a wet venturi scrubber and an entrainment separator.	There is no pollution control equipment on the prill tower other than pH and temperature controls to minimize emissions.	NA	Ammonia gas evolved from NH_3 liquid storage tanks is reliquified and recovered by refrigeration compressors. In the event of a long power failure, vent gases from the storage tanks are passed through a water scrubber.
In the concentrator (83 to 92%), the vapour is washed with water (barometric condenser) and inerts are removed by an ejector to the atmosphere. Concentration from 92 to 99% is accomplished in an air-swept evaporator. Vent gases pass through a venturi scrubber before being vented to the atmosphere.	Air-swept evaporators are vented directly to the atmosphere.	The combined neutralizer, evaporator, and prill tower vent gas streams pass through a Brinks scrubber.	No pollution control equipment.	Any vapours released from storage tanks are compressed and condensed and the liquid returned to the tank. Vapours from tank cars are chilled and separated. The liquid is returned to the storage tank and the vapours are burned in a flare stack.
No pollution control equipment. All vapours are condensed.	Off gas from the concentrator is fed to the ammonium nitrate neutralizer.	A Cooperative Farm Chemicals Association cone was installed to segregate the air immediately around the spray nozzles. In conjunction with the cone, a Brinks unit was installed to collect microprills (around 98% efficiency) and reduce opacity. Effluent from the Goodpasture units goes to the Brinks units.	The exhausts on the top of the prill tower were blocked off and the cooling air is collected by plenum chambers and directed to a CHEAF filtration unit. The recovered material is recycled back to the process.	No pollution control equipment installed.
NA	Process condensate from evaporators goes to a treatment system. The separated NH_3 and CO_2 are recycled to the low pressure recovery unit and thus to synthesis. The treated condensate is used in the granulator scrubber.	NA	NA	The main storage tank has a pressure relief valve venting to a flare. The vacuum relief valve is open to the atmosphere. The flare stack has a pilot light to ensure combustion of any ammonia vapours. A refrigeration unit compresses NH_3 vapour from storage tanks to maintain the required pressure to vent gases from loading facilities vented through the flare.

TABLE 19 AIR POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS (Cont'd)

Plant	Liquid Storage Tanks, Nitric Acid Plant	Liquid Storage Tanks, Ammonium Nitrate Plant	Liquid Storage Tanks, Urea Plant	Solid Product Storage and Loading Area Emissions, Ammonium Nitrate Plant	Solid Product Storage and Loading Area Emissions, Urea Plant
Western Co-op Fertilizers, Medicine Hat	No pollution control equipment is considered to be necessary as storage is preceded by passage through an auxiliary bleach tower.	NA	NA	No pollution control equipment.	NA
Sherritt Gordon, Fort Saskatchewan	NA	NA	Pressure relief valves in the carbamate recycling circuit are steam purged continuously to prevent blockage. The steam is contaminated with NH_3 and passes through a water knockout trap before being vented to the atmosphere.	NA	There is no pollution control equipment on the bucket elevators, coating drum, or screens or in the loading area, etc.
Simplot Chemical, Brandon	All product is used on-site. No pollution control equipment on storage tanks.	No pollution control equipment on storage tanks due to negligible losses.	Ventilation ducts carry water vapour and NH_3 gas from urea surge tanks to a venturi neutralizer scrubber. Recovered product is used in solution plant to make liquid fertilizer.	Dust from the loading facility is collected in a baghouse.	No pollution control equipment installed. Product is formulated to minimize dusting.
CIL, Courtright	No pollution control equipment on storage tanks. All acid is consumed on-site.	No pollution control equipment on storage tanks.	No pollution control equipment on storage tanks.	No pollution control equipment.	No pollution control equipment.
Cyanamid of Canada, Niagara Falls	No pollution control equipment installed.	No pollution control equipment installed.	No pollution control equipment installed.	Dust from storage and loading areas is collected in a baghouse.	Dust from storage and loading areas is collected in a baghouse
Cominco, Carseland	NA	NA	Vents from the storage tanks are connected to an evaporative scrubber.	NA	The urea is stored in a single building. Because the product is made dust free by using formaldehyde, there is no vent system within the storage building. Any lumps, fines, and spills evolving during reloading are returned as solution to the urea plant.

Relief Valve Emissions	Emissions from Sulphur Coated Urea Area	Ammonium Nitrate Plant - Dryer, Cooler	Urea Granulator	Ammonium Sulphate Crystallizers	Ammonium Sulphate Dryers and Screens
Relief valve emissions to the atmosphere occur only during start-ups and shut-downs.	NA	The airstream from the product cooler goes to a Rotoclone dust scrubber. The airstream from the product coating drum and conveyor points goes to a dust tumbler.	NA	NA	NA
All pressure relief valves in the gas reform plant and the synthesis section vent directly to the atmosphere. No pollutants are released to the atmosphere under normal conditions.	NA	NA	NA	The vacuum is created by condensing vapours from the third effects in water-cooled surface condensers. Uncondensed vapour is withdrawn from the condensers by two sets of steam ejectors.	Exhaust gases from the dryers pass through cyclone separators to separate entrained dust, which is redissolved and recycled. The gases are discharged into the feed storage tank and then to the atmosphere.
No pollutants are released to the atmosphere under normal conditions.	NA	Air drawn through the ammonium nitrate cooler is sent to a wet scrubber. Dust from the coater is collected in a baghouse.	Cooling air drawn through the granulator is scrubbed and neutralized in a venturi scrubber and entrainment separator before being released to the atmosphere. The solution is recovered and used to make liquid fertilizers.	NA	NA
Most pressure relief valves are twinned, facilitating immediate correction of a failure; thus, emissions from these sources are negligible.	Reported to be low. No information available.	The exhaust from the cooler goes to a wet scrubber. The scrubber solution bleed is recycled to process.	NA	NA	NA
All vessels and lines that could be isolated have protection. Discharge from any relief valve is to the atmosphere; however, losses are estimated to be zero.	NA	The exhaust from the predryer, dryer, and cooler goes to cyclones. The solids collected go to a weak liquor tank. The exhaust from the cyclones, containing fines, goes to a wet scrubber before being exhausted to the atmosphere.	NA	NA	NA
Relief valve on main storage tanks is vented to a flare. Vent gases from the loading facilities are also vented through a flare.	NA	NA	An impingement-type wet scrubber clean the air streams from the granulators. The condensate fed to the scrubber dissolves the dust, and concentrated solution which is recycled for reconcentration. The scrubbed air then passed through an evaporative scrubber.	NA	NA

TABLE 14 AIR POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS (Cont'd)

Plant	Purge Gas from Synthesis Loop	Carbon Dioxide Regenerator	Tail Gas from Nitric Acid Plant	Neutralizer, Ammonium Nitrate Plant	Reactor Effluent, Urea Plant
Esso Chemical, Redwater	The purge gas from plant No. 1 is used as fuel in the catalytic combustor in the HNO_3 plant. The purge gas from plant No. 2 passes through an absorber and molecular sieve to remove NH_3 and then goes through a cryogenic process to recover hydrogen, thereby increasing the production rate.	The by-product carbon dioxide is used in the production of urea. The remainder is vented to the atmosphere.	The tail gas passes through a catalytic combustor containing platinum gauze.	The reaction is exothermic and produces quantities of steam that may contain particulates, ammonia, and HNO_3. This plant controls these emissions by total condensation.	No effluent.
Nitrochem Inc., Maitland	No purge gas.	The by-product carbon dioxide is partially recovered in a liquid carbonic acid plant. The remainder is vented to the atmosphere.	Plant No. 1 - The absorber tail gas and natural gas go to a catalytic combustor (decolorizer), to a power recovery unit, and then to Gulf's molecular sieve abatement system. Plant No. 2 - The tail gas and natural gas are fed to a dual catalytic converter. Plant No. 3 - The tail gas and natural gas go to a direct-fired heater, followed by a catalytic converter.	The exhaust gases from the neutralizer, containing ammonia and ammonium nitrate, are condensed. The condensate is steam stripped to remove ammonia.	NA
Canadian Fertilizer Ltd., Medicine Hat	The purge gas is used as part of the fuel required for the radiant heat section of the primary reformer.	The by-product carbon dioxide is used to manufacture urea. The remainder is vented to the atmosphere.	NA	NA	Unreacted ammonia water vapour and particulates from the reactor go to a high pressure water scrubber. The effluent is recycled via a high pressure condenser to the reactor. Gases are vented to the atmosphere from the scrubber.
Cominco, Calgary	Used as fuel in the boiler house.	The by-product carbon dioxide is used to produce urea. The remainder is vented to the atmosphere.	Extended absorption for NO_x removal and use of most of the tail gas for NH_3 production.	York demisters are installed on the neutralizer stack.	All reaction products and off gas go to a primary decomposer, secondary decomposer, and absorber, and the ammonia is compressed and recycled to process.
Cominco, Trail	Purge gas is scrubbed in packed towers using condensate to recover NH_3. The weak NH_3 solution is reused in another plant. The gas, containing hydrogen, some methane, and inerts, is discharged to the atmosphere.	The by-product carbon dioxide is vented to the atmosphere.	NA	NA	NA
Western Co-op Fertilizers, Calgary	Part of the purge gas is used in the nitric acid catalytic converter system. Ammonia is first removed in a purge gas scrubber. The remainder is used as fuel in the primary reformer.	The by-product carbon dioxide is recovered in a liquid CO_2 plant. Some is vented.	Catalytic converter system used.	The steam containing particulates, ammonia, and HNO_3 exiting from the neutralizer goes to a fume scrubber followed by a neutralizer condenser.	NA

Concentrator, Ammonium Nitrate Plant	Concentrator, Urea Plant	Prill Tower Vent Gas, Ammonium Nitrate Plant	Prill Tower Vent Gas, Urea Plant	Liquid Storage Tanks, Ammonia Plant
The vapour from the evaporator goes to a wet scrubber. The exhaust goes to the atmosphere. The scrubbing liquor goes to the dissolving tank.	The separated NH_3 and CO_2 are recycled to the low pressure recovery unit and thus to synthesis. The process condensate is treated and used in the granulation scrubber.	Quiet zone at prill pots allows fallout. A Brinks filter fume eliminator is installed on the tower vent.	NA	Vent gases are returned via a refrigeration unit to the storage tank.
The vent gases from the concentrator, which contain ammonia and ammonium nitrate, are condensed. The condensate is steam stripped to remove ammonia.	NA	No pollution control devices.	NA	No pollution control equipment installed.
NA	The rectifying column, 1st desorber flash tank, and off gas from two evaporators are vented to a low pressure water scrubber to remove ammonia and particulates.	NA	NA	Ammonia tank vapours are returned to the refrigeration system via the compressors. Vapours from the loading dock are returned to the ammonia tanks or are burned.
The vapour from the evaporator is washed with water (barometric condenser) and inerts are removed by an ejector to the atmosphere.	The ammonia vapour and entrained particulates from the two evaporators are captured in an impinger scrubber, which is followed by a demister.	No pollution control equipment. Low losses reported from low density prill tower.	NA	Any vapours released from storage tanks are compressed and condensed, and the liquid is returned to the tank.
NA	NA	NA	NA	All gas is continuously recycled to a low pressure gaseous system. This gas is compressed, condensed, and stored as low pressure liquid NH_3.
Vapour from the evaporator is washed in a scrubber system before venting to the atmosphere.	NA	A Brinks scrubber collects microprills from the spray nozzle discharge area.	NA	All controlled ammonia venting is flared. There is a compression/recycle system on the low pressure storage tanks.

TABLE 19 AIR POLLUTION CONTROL MEASURES AT NITROGEN FERTILIZER PLANTS (Cont'd)

Plant	Liquid Storage Tanks, Nitric Acid Plant	Liquid Storage Tanks, Ammonium Nitrate Plant	Liquid Storage Tanks, Urea Plant	Solid Product Storage and Loading Area Emissions, Ammonium Nitrate Plant	Solid Product Storage and Loading Area Emissions, Urea Plant
Esso Chemical, Redwater	No pollution control equipment.	NA	No information available.	Emissions from some screens, transfer points, and certain areas are collected in a bag collector.	Reported to be low. No information available.
Nitrochem Inc., Maitland	No pollution control equipment.	No pollution control equipment.	NA	Emissions from some screens and transfer points are collected in a bag collector.	NA
Canadian Fertilizer Ltd., Medicine Hat	NA	NA	NA	NA	No pollution control equipment.
Cominco, Calgary	Vented into NH_3 line to nitrate neutralizer.	No pollution control equipment.	No pollution control equipment.	Emissions from transfer points and conditioner are collected in a baghouse. The fines collected are sold.	Emissions from transfer points are collected in a baghouse.
Cominco, Trail	NA	NA	NA	NA	NA
Western Co-op Fertilizers, Calgary	Nitric acid storage tank vents are tied into the nitric acid exhaust stack to promote dispersion.	No pollution control equipment.	NA	No pollution control equipment.	No information available.

Note: NA, not applicable

Relief Valve Emissions	Emissions from Sulphur Coated Urea Area	Ammonium Nitrate Plant - Dryer, Cooler	Urea Granulator	Ammonium Sulphate Crystallizers	Ammonium Sulphate Dryers and Screens
There is standby refrigeration for any relief valve exhaust gases.	NA	The exhaust from the cooler is sent to a wet scrubber.	A wet scrubber cleans the air-stream from the granulator. The exhaust from the scrubber goes to a stack. The scrubber solution is recycled with a bleed-off to the concentrator separator.	NA	NA
No pollution control devices.	NA	Emissions from the predryer and dryer go to a wet scrubber. The weak ammonium nitrate solution is recycled to the neutralizer.	NA	NA	NA
No information available.	NA	NA	Because up to 20% of the product can be entrained in the cooling air, water scrubbers are used. The exhaust goes to the atmosphere. The solution is recycled to the evaporator.	NA	NA
Periodically vented to the atmosphere.	NA	Emissions from the dryer go to a wet cyclone. The cyclone exhaust goes to the atmosphere.	Ammonia and dust emissions from the granulator go to a Tubulaire Doyle scrubber.	NA	NA
The relief valves in the reforming section, in the premethanator, ahead of the compressor, and in the header vent at the syn gas plant are periodically vented to the atmosphere.	NA	NA	NA	A vacuum is maintained in an overhead vent by a condenser using reclaimed water. This water plus some ammonium sulphate carryover goes to the sewer. Foam from the crystallizers and centrifuge goes to spray eliminators. The effluent goes to the sewer.	The exhaust from the dryer goes to a wet cyclone. The underflow goes to the crystallizer. The overhead is scrubbed; the effluent goes to the sewer. The vent from the screens goes to a wet cyclone. The underflow goes to a dissolving tank. The overheads are scrubbed. The effluent goes to the dissolving tank. For ventilation of bagging and bulk loading systems, cyclones and baghouses are used.
Venting to the atmosphere occurs only during upsets or the occasional start-up.	NA	A Rotoclone (wet cyclonic scrubber) recovers dust losses from the product cooler. A baghouse recovers dust losses from the coater and bucket elevator.	NA	NA	NA

TABLE 20 AIR EMISSIONS FROM NITROGEN FERTILIZER PLANTS

Plant	Nitric Acid Plants		Ammonia Plants					Ammonium Nitrate Plants	
			Reformer Stack		CO_2 Regenerator				
	NO_2 (kg/d)	NO_2 (t/yr)	NO_2 (kg/d)	SO_2 (kg/d)	CO_2 (t/d)	NH_3 (kg/d)	Hydrocarbons (kg/d)	NH_3 (kg/d)	Particulates (kg/d)
CIL, Courtright	120	42	1457	1.5	100 (from NH_3 plant)	-	-	210	186
Cyanamid of Canada, Niagara Falls	2700	890	NIA	0.6	310	255	120	450	400
Nitrochem, Maitland	1014	365	NIA	NIA	154	125	60	405	490
Canadian Fertilizer, Medicine Hat	NA	NA	No emission figures supplied.						
Cominco, Calgary	67	23.5	889	- 128 (NH_3)	17	14	7	45	435
Cominco, Carseland	NA	NA	4500	-	96.9	0.05	NIA	NA	NA
Cominco, Trail	NA	NA	NIA	1.85	230	190	90	NA	NA
Esso Chemical, Redwater	950	315	3865	NIA	900	1100	500	185	320
Sherritt Gordon, Fort Saskatchewan	NA	NA	NIA	NIA	NIA	NIA	NIA	NA	NA
Simplot Chemical, Brandon	605	211.7	NIA	NIA	40	330	165	500	247
Western Co-op, Calgary	360	122	164	NIA	200	2.8	0	6	103
Western Co-op, Medicine Hat	NA	NA	948	NIA	NIA	NIA	NIA	NA	NA

Note: Nitrochem has an emission of 9000 kg/d CO and 2500 kg/d CH_4 from its nitrogen scrubbing unit
NIA, no information available
NA, not applicable

Urea Plants		Nitrogen Solution	Ammonium Sulphate Plant		Sulphur Coated Urea			Boiler House Stack
NH_3 (kg/d)	Particulates (kg/d)	NH_3 (kg/d)	NH_3 (kg/d)	Particulate (kg/d)	Particulate (kg/d)	Urea (kg/d)	Sulphur Wax Clay (kg/d)	NO_2 (kg/d)
3600	1365	NIA	NA	NA	76	50	26	NIA
500	0.2	5 (air-swept concentrators)	NA	NA	NA	NA	NA	NIA
NA	NA	1200 (estimated)	NA	NA	NA	NA	NA	NIA
		NIA	NA	NA	NA	NA	NA	NIA
590	135	NA	NA	NA	NA	NA	NA	315
4225	48	NA	NA	NA	NA	NA	NA	589
NA	NA	NA	19	85	NA	NA	NA	NIA
1400	1000	NA	NA	NA	NA	NA	NA	NIA
2600	1375	NA	NIA	Negligible	NA	NA	NA	NIA
1500	70	Negligible (estimated)	NA	NA	NA	NA	NA	NIA
NA	NA	NIA	NA	NA	NA	NA	NA	NIA
NA	NA	NIA	NA	NA	NA	NA	NA	NIA

Fuel for Reformer		Fuel for Boiler House	To HNO_3 Catalytic Converter	Recovered by Cryogenic Process	To Atmosphere After NH_3 Recovery
As Purged	With NH_3 Removed				
5.5 plants*	1 plant	2 plants	1 old plant** 0.5 plant*	1 new plant** 1 plant	1 plant

* part of the purge gas goes to the acid plant, the remainder goes to the primary reformer

** both plants form part of the same complex

Vent gas. Vent gases from relief valves from certain areas in the plant usually go to the atmosphere; however, under normal conditions there are no releases. Vent gases from storage tanks are reported as being refrigerated, condensed, and sent back to storage. Under emergency situations, the ammonia is either vented through a tall stack or flared.

Ammonium nitrate plants. Seven plants in Canada currently produce ammonium nitrate (one plant is temporarily closed). The major emission sources of ammonia and particulates are the neutralizer, evaporator, prill tower, and coolers and dryers. Nitric acid vapour emissions are normally nil or very minor.

Neutralizer emissions are reported as being controlled by a York demister (one plant), a demister followed by a Brinks scrubber (one plant), condensation (three plants), a wet cyclonic spray scrubber (one plant), and a scrubber followed by a condenser (one plant). Reported ammonia emissions were in the range of 0 to 0.85 kg of NH_3 per tonne of product produced, with the average being 0.48 kg/t. Particulate emissions ranged from 0 to 2.5 kg per tonne of product, with the average being about 0.27 kg/t.

Evaporator emissions were reported as being controlled by wet scrubbers (two plants), scrubbing followed by a total condenser (one plant), condensation (one plant), and discharging the exhaust to a stack (three plants).

Of the plants that reported emission levels, the ammonia discharges ranged from nil to 0.23 kg per tonne of product, with the average being about 0.10 kg/t. Particulate emission data were not considered sufficient to warrant inclusion.

The prill tower discharge air, contaminated with ammonia, ammonium nitrate fume, and dust, is vented through Brinks scrubbers at four plants. The discharge air from

the towers at the other three plants goes directly to the atmosphere; however, these towers have pH and temperature controls to minimize emissions. Reported ammonium nitrate dust emissions ranged from 0.11 to 7 kg per tonne of product, the average being 0.80 kg/t. Only one plant reported ammonia emissions of 0.10 kg/t.

Only two plants reported dust emissions, from dryers and loading facilities, at 0.02 and 0.03 kg per tonne of product. This information is insufficient to calculate an emission factor; however, on the basis of these two results and data from the literature, emissions from dryers, screens, etc. are considered insignificant.

Nitric acid plants. Information from the plants surveyed indicates that seven plants are currently producing nitric acid in connection with the fertilizer industry in Canada. (One plant is temporarily closed.)

One plant site has three units: one unit uses a catalytic converter followed by a molecular sieve, another unit uses a dual catalytic converter, and the third unit has a catalytic converter. Four other plant sites use catalytic reduction to convert NO_x to N_2. One other plant uses extended absorption, with the tail gas being used for ammonia production. The remaining plant also has three units, with the tail gas going to a Goodpasture chemical abatement system.

All plants report NO_x emissions as equivalent NO_2 at less than 6 kg per tonne of 100% nitric acid produced; the average for the seven plant sites being 2.14 kg per tonne of acid.

Urea plants. Eight plants in Canada are currently producing urea. The major emissions of concern are ammonia and particulates. Four and one half of the eight plants (one plant site has an older and a newer installation) use granulators to solidify the urea. All four and one half of the plants use wet scrubbers to control ammonia and particulates. Ammonia and urea emissions from the control equipment averaged 1.45 and 0.32 kg per tonne of urea produced respectively.

The remaining 3.5 plants use prilling towers. Reported ammonia and particulate (urea) emissions averaged 1.2 and 0.50 kg per tonne of urea produced respectively. One of these prill towers has a CHEAF scrubber on the tower exhaust. The reported ammonia and particulate emissions from this control unit are 0 and 6.4×10^{-4} kg per tonne of urea produced respectively.

Ammonia and particulate emissions originating from the evaporator/concentrator averaged 1.4 and 0.58 kg per tonne of urea produced respectively.

The annual nationwide emissions for the nitrogen fertilizer industry are estimated at 14 500 t of ammonia and 4000 t of particulate urea. The ammonia emissions refer to total emissions from all sources, whereas the particulate losses are from the evaporators/concentrators, prill towers, and granulators.

No particulate emissions were reported from other sources, such as screens, bucket elevators, loading facilities, etc.; however, on the basis of the information collected, these emissions are considered insignificant.

8.2 Phosphate Fertilizer Industry

This subsection deals with various approaches employed by the phosphate fertilizer industry to control and treat air emissions. The first part outlines the various types of wet scrubbers used by the phosphate industry and their operating characteristics. The subsequent parts indicate the types of control equipment used in the various processes.

8.2.1 Available Technology.

Types of scrubbers used in phosphate fertilizer plants. Phosphate fertilizer manufacturing processes start with phosphate rock acidulation, which results in gaseous fluoride (primarily HF and SiF_4) and particulate emissions. In general, the extent of the fluoride abatement equipment is determined by the inlet F concentration and F compounds present, the outlet F concentration goal, the gas temperature, the liquor temperature and composition, the effectiveness of the scrubber, and entrainment separation. The overall efficiency of particulate and/or aerosol collection in wet scrubbers is influenced mainly by the particle or aerosol size (the larger the size, the higher the collection efficiency), pressure drop (in general, the higher the pressure drop, the higher the collection efficiency), and liquid-to-gas ratio. Because wet scrubbers can simultaneously remove both particulate and gaseous emissions, their use in the phosphate fertilizer industry is widespread.

Spray - cross-flow packed bed scrubber (50). The spray - cross-flow packed bed scrubber consists of two sections, the spray chamber and a packed bed, separated by irrigated baffles (Figure 28). Both sections are equipped with gas inlets. Effluents with high fluoride and particularly high SiF_4 concentrations move horizontally through the spray chamber before entering the packing. This reduces the danger of plugging in the bed, reduces the loading on the packed stage, and provides some solids handling capacity. Solids deposited near the front of the bed are washed off by a cleaning spray and the

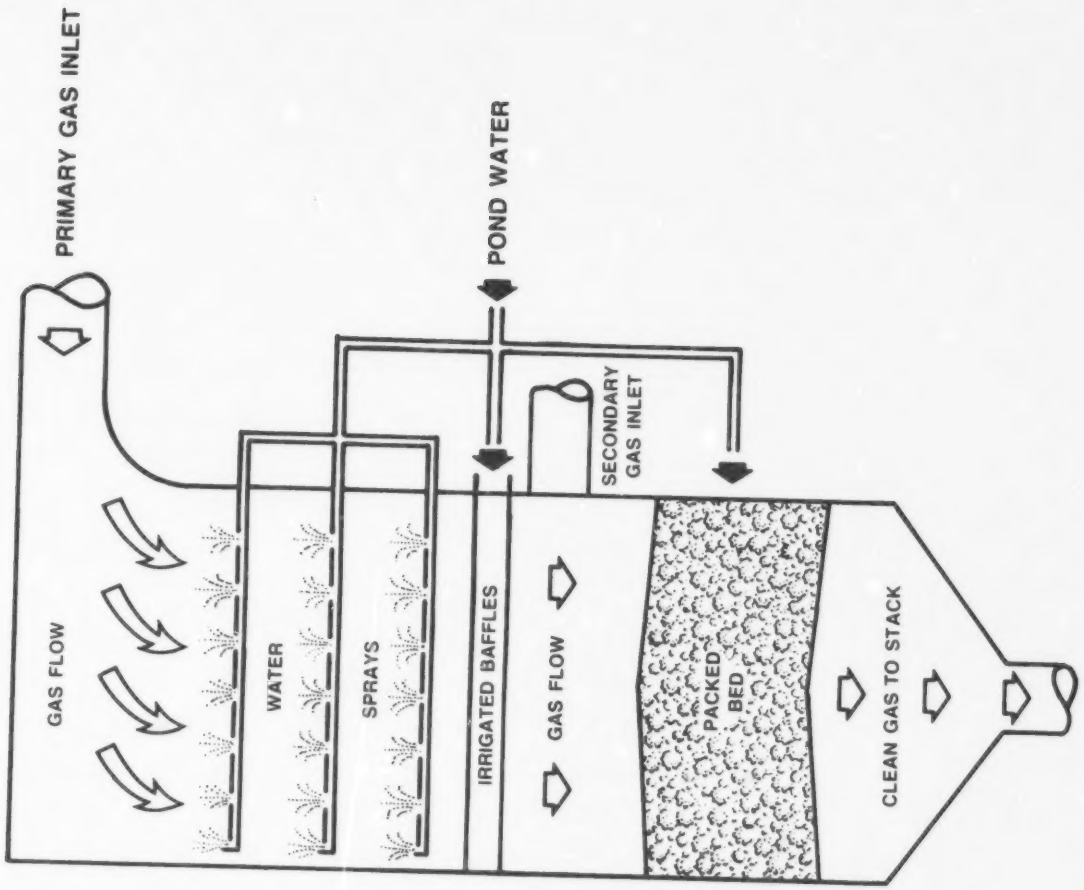


FIGURE 28 SPRAY - CROSS-FLOW PACKED BED SCRUBBER

scrubbing liquor flowing vertically through the packing. Recycled gypsum pond water is normally used as the scrubbing liquor. The pressure drop across the scrubber is relatively low.

Cyclonic spray scrubber (50). Spray towers provide the contact necessary for gas absorption. The centrifugal force is generated by the tangential dirty gas inlet as shown in Figure 29. The liquid is sprayed radially outward from nozzles on a central pipe.

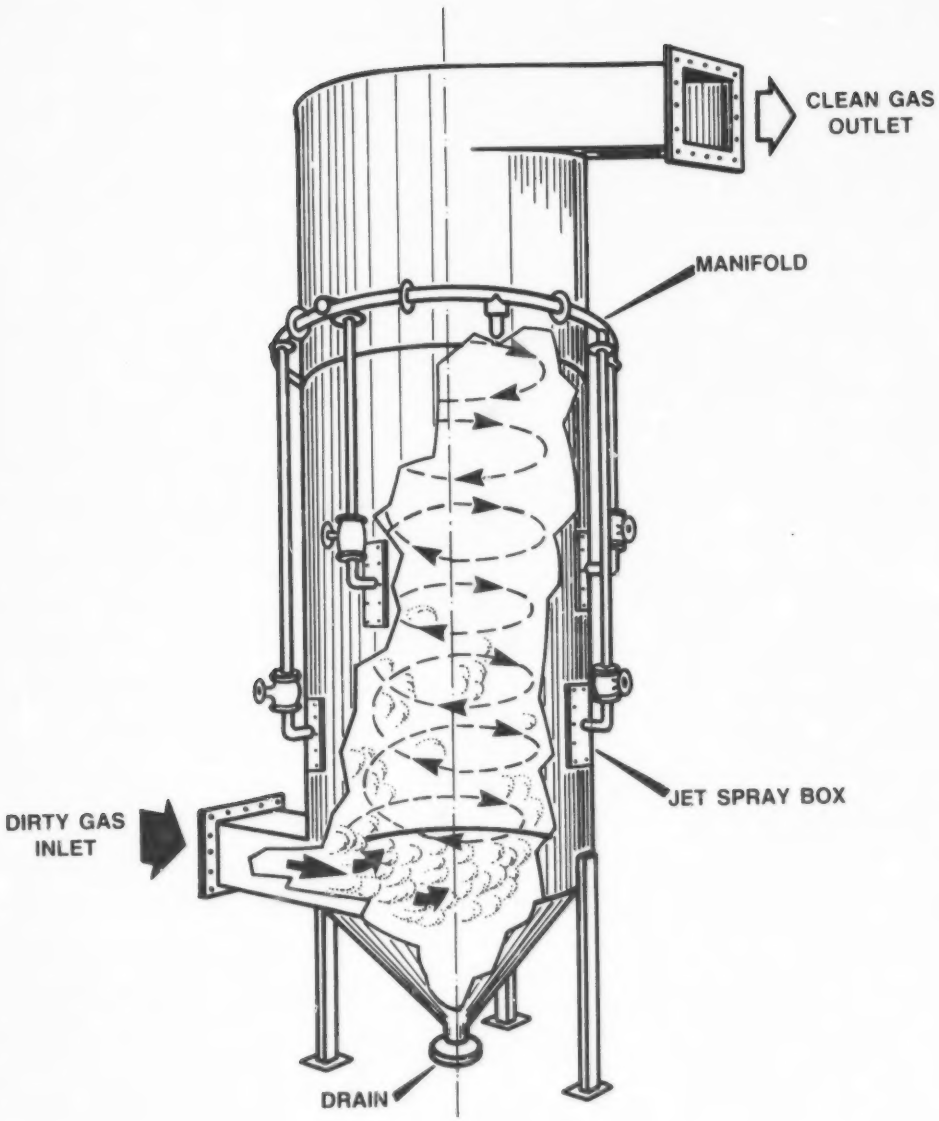


FIGURE 29 CYCLONIC SPRAY TOWER SCRUBBER

This type of scrubber eliminates excessive entrainment of scrubbing liquor by utilizing centrifugal force to remove entrained droplets. The Ducon Company scrubber uses swirl vanes to supplement the centrifugal suction generated by the tangential inlet. The spray is directed vertically downward.

Venturi scrubbers (50). The venturi scrubber provides a high degree of gas-liquid mixing, but the relatively short contact time limits its absorption capabilities so it is used primarily for particulate removal. The gas-activated venturi uses the velocity of the gas stream as the source of energy for liquid atomization and contact. The necessary gas-liquid contact is achieved from the velocity difference between the two phases and turbulence in the throat. The water-activated venturi uses the velocity of the water stream as a source of energy. Both types also require the use of mist eliminators for removing entrained scrubbing liquor.

Coaxial scrubber (50). The Teller coaxial scrubber is shown in Figure 30. The liquid flow enters the top and is distributed primarily by underflow weirs; thus, deposition of solids does not usually take place. The venturi throat is diamond shaped to minimize scaling. This scrubber, with a high scrubbing efficiency, is used for ammonia absorption with phosphoric acid.

Impingement scrubbers. The impingement scrubber consists of a perforated sheet with impingement baffles arranged so that a baffle is located directly above each perforation. The gas enters the spray tower base where the coarse dust is removed. The sprays also serve to irrigate the bottom of the first plate to minimize deposits. The gas velocity through the holes is 20 to 30 m/s. This atomizes the liquid into droplets on the order of 100 µm in diameter. These droplets are the effective collecting bodies in the scrubber.

Raw material handling. Satisfactory control of dust emissions from phosphate rock unloading equipment is achieved by using flexible skirts around the base of the equipment to contain dust and flexible contact hoods to vent emissions to baghouses. Hoppers, storage bins, and conveyors are normally enclosed to reduce dust emissions. The ground rock is usually conveyed to the feed storage bin by pneumatic conveyors. A cyclone separator and baghouse are located above the bin to control the bulk material and discharged dust. Baghouses realize high collection efficiency of this size of particle (60% < 74 µm).

Wet process phosphoric acid (WPPA). One of the most effective scrubbing systems available to control fluoride emissions from WPPA plants is the spray - cross-flow

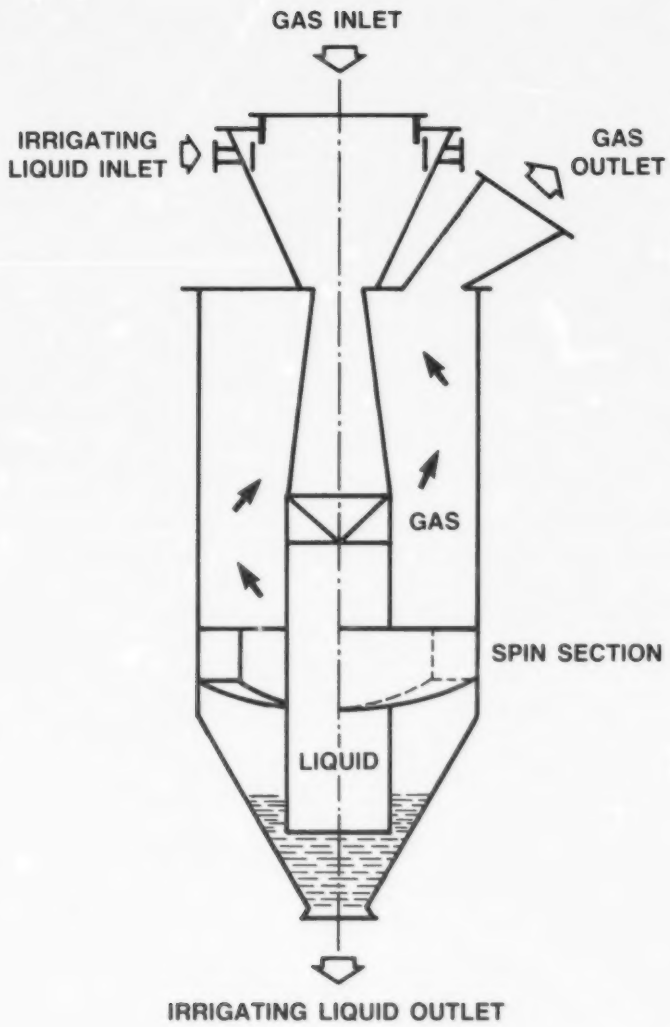


FIGURE 30 TELLER COAXIAL SCRUBBER

packed bed scrubber. A venturi scrubber can be used in series before the spray - cross-flow packed bed unit for gas streams that have a high solids content.

If fluorides are to be recovered as marketable fluosilicic acid, a different sequence may be used, e.g., the gases from the acidulation reactor, filter, and seal tanks might go to a spray - cross-flow packed scrubber. Gases from the vacuum cooler and vacuum evaporators might go to a low pressure drop scrubber. The scrubbing water from the reactor-filter scrubber is used in low pressure drop scrubbers, finally leaving the scrubbers as by-product H_2SiF_6. Gases from the low pressure scrubber go to a barometric condenser to collect any remaining fluorides.

Normal superphosphate (NSP). Emissions of fluorides and particulates from the mixer, den, and curing building are controlled by a wet scrubbing system using recycled water. Overall fluoride emissions can amount to between 10 and 50% of the fluoride in the rock; thus, 2 to 11 kg of F will be released per tonne of product. NSP is not being produced in Canada at present.

Triple superphosphate (TSP). Fluoride and particulate emissions from the manufacturing of granular triple superphosphate and run-of-the-pile triple superphosphate are controlled by a wet scrubbing system. A typical system would include a venturi scrubber to remove particulates, followed by a cyclonic scrubber for fluoride removal, and a third stage spray scrubber to improve the overall scrubbing efficiency. An alternative system might use a venturi scrubber followed by a spray - cross-flow packed scrubber. Fluoride emissions can amount to between 32 and 40% of the fluoride in the rock, or 5 to 6 kg per tonne of product. At present, TSP is not being produced in Canada.

Ammonium phosphate. Gases with entrained solids from the preneutralizer and granulator first go to a wet scrubber where most of the ammonia is absorbed in dilute phosphoric acid. Residual ammonia leaves the scrubber as gaseous NH_3 or as submicron particulate ammonium fluoride or bifluoride. Some solids and entrained phosphoric acid will also leave the scrubber. The type of scrubber used in this first stage scrubbing process can vary from plant to plant but normally includes venturi scrubbers, two-stage cyclonic scrubbers, or a spray tower.

The gases from the first stage scrubber go to second stage wet scrubbers where ammonia, solids, and fluorides are further removed in the scrubbing liquor. These second stage scrubbers also vary from plant to plant but could include impinger scrubbers, venturi scrubbers, ring and cone scrubbers, or two-stage cyclonic scrubbers. Some plants have a third bank of scrubbers to further reduce NH_3, fluoride, and particulate emissions.

Some of the plants in the U.S. use a venturi scrubber followed by a two-stage spray - cross-flow packed bed scrubber (50).

Gases and particulates from the dryer, cooler, screens, and conveyors are normally treated in a dry cyclone (to remove the bulk of the solids) followed by a scrubbing system similar to that described for the preneutralizer and granulator gases.

Sulphuric acid plants. Until recently, the only method of control applied to the emission of sulphur dioxide and acid mist from a sulphuric acid plant was dispersion. Some plants have converted to the double absorption process, which can attain an efficiency of up to 99.5% on a continuous running basis. This implies an SO_2 concentration of around 500 ppm in the tail gas. If levels of 200 ppm are expected, then some form of tail gas treatment will be necessary. This treatment could include the Wellman-Lord process, ammonia scrubbing, and mist eliminators.

Wellman-Lord process (51). In this process, the SO_2 is absorbed in a sodium or potassium sulphite solution to form sodium or potassium bisulphite, which is subsequently regenerated and the liquor is recycled. A small amount is oxidized to nonregenerable sulphate, which must be bled off for disposal. If potassium sulphite is used, the bled-off potassium sulphate can be used as a fertilizer. The cost of this tail gas treatment is very high, particularly for a small plant.

Ammonia scrubbing (52). The ammonia scrubbing process uses anhydrous ammonia in water in a two-stage scrubbing system. Excess ammonium sulphite-bisulphite solution is stripped with H_2SO_4 to evolve SO_2 gas and produce ammonium sulphate. The SO_2 is recycled to the plant and the $(NH_4)_2SO_4$ is used as a fertilizer.

Mist eliminators (52). Acid mist carryover can be minimized by careful control of conditions in the absorption tower. Control equipment must be installed, however, to ensure that very low quantities of mist are emitted under all operating conditions. When horizontal mesh pads, glass fibre packed vertical tubes, or vertical fibre panels are used, large droplets are formed, which return to the absorption tower by gravity. The horizontal pads are not effective for very small droplets. High efficiency for droplets less than 0.003 mm in diameter can be achieved, however, with glass fibre mist eliminators. Electrostatic precipitators are also efficient but they are expensive and are difficult to maintain.

8.2.2 Air Emission Control Measures. The emissions of most concern in the phosphate fertilizer industry are gaseous fluorides and particulates. Wet scrubbers are

normally used to control them. It has been found that a scrubber that effectively controls gaseous fluoride emissions will also effectively control particulates (fluorides and rock).

This section deals with the various methods used by the Canadian phosphate fertilizer industry to control air emissions from process and control equipment. Existing control methods are summarized in Table 21. Table 22 shows the major contaminants emitted from phosphate fertilizer plants in Canada. Most of the data are supplied by industries and, because of differences in sampling and analytical procedures, direct comparison between plants should be approached with caution. In this report, the fluoride value referred to is the weight of the fluorine and does not include the chemically combined elements.

Phosphate rock handling. Six Canadian phosphate fertilizer producers are currently digesting phosphate rock to produce phosphoric acid. One plant is temporarily closed. Another plant ceased operations in 1986.

Five of the six plants use baghouses to control dust emissions associated with rock preparation and handling. One other plant uses a wet impinger scrubber. Collected fines in all cases are recycled to the process. One phosphate fertilizer producer purchases phosphoric acid and, consequently, does not handle phosphate rock. As noted in Table 22, many of the plants do not have data on dust emissions.

Phosphoric acid. Six phosphate fertilizer plants in Canada manufacture phosphoric acid as an intermediate, with production ranging from 50 000 to 270 000 t of P_2O_5 equivalent per year. Five of the plants combine the emissions and treat them in a cross-flow packed scrubber, a treatment the U.S. Environmental Protection Agency recommends as the best technology. Reported emissions ranged from 0.004 to 0.113 kg of fluoride per tonne of P_2O_5 equivalent, with the average being 0.028 kg/t. The remaining plant uses two impinger scrubbers in series. Fluoride emissions from this plant average 0.17 kg per tonne of P_2O_5 equivalent. Most scrubbers use recycled pond water as the scrubbing liquor. However, one plant uses seawater, whereas another uses both ammonia plant wastewater and raw water.

Annual fluoride emissions from the production of phosphoric acid are estimated at 31 t. From the limited data available, the annual particulate and phosphate emissions from the production of phosphoric acid are estimated at 49 and 2.5 t respectively.

Ammonium phosphate. Six phosphate fertilizer plants in Canada are currently producing ammonium phosphate. Reactor emissions are generally controlled by wet

TABLE 21 AIR POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS

Plant	Phosphate-Rock Grinding Mill	Phosphate Ground-Rock Storage Bin	Phosphoric Acid Reactor Vessel
Esso Chemical, Redwater	The ball mill dust is drawn by a fan to the storage bin.	The air is drawn from the storage bin through a bag collector. The filtered air is exhausted to the atmosphere via a stack. The fines are returned to the bin.	The reactor is air swept to a cross-flow scrubber containing pond water sprays, baffles, and packing. The scrubber is exhausted to the atmosphere and the liquid is recycled to the gypsum pond.
Sherritt Gordon, Fort Saskatchewan	Ground rock is conveyed pneumatically from the ball mill discharge to the classifier. The coarse particles are recycled. The fines pass to a cyclone. The underflow goes to the storage bin. The exhaust from the cyclone is recycled to convey more rock with a purge going to a bag collector.	The air is drawn from the storage bin through a bag collector. The filtered air is exhausted to the atmosphere via a stack. The fines are returned to the bin.	The system is equipped with a Teller scrubber to vent the reactor vessel, filtrate seal tank, flash cooler seal tank, and filter vacuum scrubber seal tank.
International Minerals and Chemical Corporation Ltd.	This plant is closed at present.		
Cominco, Kimberley	Particulate emissions from the grinding mills are controlled by keeping the mills under suction and passing the ventilated gases through dry cyclones and impinger scrubbers. The solids in the water settle out in ponds. The solids are eventually reclaimed.	The storage bins are ventilated via impinger scrubbers. The solids are reclaimed. The rock dryer is ventilated via dry cyclones and impinger scrubbers. The solids are reclaimed.	The reactor ventilation gases are scrubbed with recycled gypsum pond water in two impinger scrubbers in series. The collected material goes to the gypsum ponds.
Belledune Fertilizer	Ground rock is conveyed pneumatically from the ball mill discharge/fluidizer to a cyclone. The recovered dust goes to a silo. Excess air and fine dust are bled from the fluidizer circuit to a baghouse. The filtered air goes to the atmosphere. There is no pollution control equipment on the bulk storage silos or conveyor belts.	The storage silo is vented to the atmosphere.	All off gases from the reactor are drawn to a Teller cross-flow scrubber where they pass through saltwater sprays and a bed irrigated with seawater. The exhaust goes to the atmosphere.

Phosphoric Acid Filter	Phosphoric Acid Storage	Barometric Condenser	Sumps and/or Acid Splitter Boxes
The air from the filter hoods and recycle acid box is ducted to a cyclone spray scrubber. The exhaust from the evaporator hot well and seal tanks also goes to this scrubber.	There is no pollution control equipment on the acid storage tanks.	No information available.	Exhaust from the sumps and acid splitter box go to the cyclone spray scrubber.
The Teller scrubber also vents the filter and filter feed box.	There is no pollution control equipment on the acid storage tanks.	The evaporator hot well is exhausted through the Teller scrubber.	The 22% acid feed box, filtrate sumps, and effluent water sump are also vented through the Teller scrubber.
The strong acid sections of the filters are vented to impinger scrubbers. The scrubbing liquor goes to the sewer. The weak acid and gypsum disposal sections are vented to the atmosphere.	The acid storage tanks are vented to the atmosphere via natural draft stacks.	The filter vacuum condensers are vented to the atmosphere via Nash pumps. Only minor amounts of contaminants escape the condensers. Any collected material goes to the sewer.	Emissions from splitter boxes are eliminated by installing solid pipe connections. Any residual emissions go to the atmosphere. Any residual emissions from sumps are collected and go to the atmosphere.
The strong acid sections of the filter are vented to the Teller scrubber.	The acid storage tanks are vented to the atmosphere.	The filter vacuum condensers are vented to the atmosphere via Nash pumps. Off gases from the evaporator go to a barometric condenser. The seawater used goes to the sewer.	Emissions from the acid splitter box and some of the sumps go to the Teller scrubber.

TABLE 21 AIR POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS (Cont'd)

Plant	Ammonium Phosphate Reactor	Ammonium Phosphate Granulator	Ammonium Phosphate Dryer
Esso Chemical, Redwater	The fumes from the reactor go to a reactor scrubber. The exhaust goes to the atmosphere; the solution goes to a seal tank with a bleed off to the reactor.	The pug mill granulator fumes containing particulates go to a cyclone and then to the reactor scrubber. The cyclone solids are recycled to the granulator.	Dust from the dryer goes to a cyclone followed by a wet scrubber. The exhaust from the scrubber goes to the atmosphere. The scrubber liquor goes to the seal tank. The cyclone fines are recycled for granulation.
Sherritt Gordon, Fort Saskatchewan	The gases (ammonia, fluoride) and dust liberated from the reaction (in the reactor) are exhausted to the fume scrubber before being discharged to the atmosphere. The scrubber liquor is recycled to the scrubber with a bleed off to the dissolution tank.	Air and fumes from the blunger are also drawn through the fume scrubber. The scrubber is an Arco jet impactor scrubber, which uses a narrow venturi throat for intimate contact between the liquid and gases.	Exhaust gases from the dryer are drawn through cyclones by a fan and then discharged through a dryer scrubber to the atmosphere. The cyclone dust is returned to the system.
International Minerals and Chemical Corporation Ltd.			
Cominco, Kimberley	The ammoniator off gas is collected and passed through three stages of scrubbers. The gas first passes through an acid spray tower, then through a baffled ring and cone scrubber to recover NH_3. The final stage is a horizontal baffled spray box.	The exhaust from the blunger also passes through the same three-stage scrubbing system. The recovered ammonia is returned to the process, as is the scrubber acid. The collected material from the third stage is returned to the process.	The dryer off gases are collected under suction and first pass through dry cyclones to remove dust, which is recycled. The gas then passes through an impinger scrubber. The acid liquor recovers the NH_3, which is returned to the process. The gas then passes through an impinger scrubber using water.
Belledune Fertilizer	The off gases containing ammonia, dust, and fluorides liberated from the reaction are vented to a venturi scrubber using phosphoric acid as the scrubbing medium. The gas then passes through a cyclonic scrubber. The stripped gas is sprayed with water, passes through a knockout drum, and then goes to the atmosphere.	The exhaust from the granulator also goes to the venturi and cyclonic scrubber. Ammonia is absorbed in the acid, which serves as feed for the reactor. Most of the dust is also captured and goes back to the reactor.	The airflow from the dryer, containing dust, fluorides, and ammonia, goes to a series of cyclones to recover the solids. The gas stream from the cyclones goes to a second venturi scrubber similar to the one used for reactor off gases.

Ammonium Phosphate Screens and Conveyors	Ammonium Phosphate Cooler	Ammonium Phosphate Coater, Elevators, etc.	Sulphuric Acid
Dust from the screens is collected in a baghouse. The fines are recycled to the pug mill.	The dust in the cooler exhaust air goes to the same cyclone and wet scrubber as the exhaust from the dryer.	No information available.	The double absorption process is used at this plant, which reduces SO_2 emission levels to a low concentration. Acid mist is reduced by using a Brinks mist eliminator.
The dust collection system draws air with entrained dust from the screens, elevators, pulverizers, fines conveyors, and storage bins through Fly Ash Arrestor Corp. cyclones followed by an Arco jet impactor scrubber. The liquor is returned to the scrubber feed tank. Scrubbed air goes to the atmosphere.	NA	The dust collection system draws air with entrained dust from the screens, elevators, pulverizers, fines conveyors, and storage bins through Fly Ash Arrestor Corp. cyclones followed by an Arco jet impactor scrubber. The liquor is returned to the scrubber feed tank. Scrubbed air goes to the atmosphere.	A double conversion - double absorption process is used, which reduces SO_2 emission levels to a low concentration. Before the gases pass to the atmosphere from the final absorbing tower, they pass through a Brinks high velocity mist eliminator, which lowers acid mist discharges.
The screens are ventilated via dry cyclones. The solids are returned to the process. An impinger scrubber then scrubs the gas with an acidic liquor. The material collected is returned to the process via the scrubber liquor system.	The cooler off gas is collected under suction and passed through a cyclone to remove the dust, which is returned to the process. The gas then passes through an impinger scrubber. The material is returned to the process.	There is no coater. There is no pollution control equipment on the elevators.	Sulphur dioxide rich gas from the roasting of iron sulphide concentrates is cleaned by passing it through gas cleaners, coolers, electrostatic precipitators, and dryers before it enters the Monsanto conversion unit and absorber.
The screens and conveyors are ventilated via the cyclones and venturi scrubber used to control emissions from the ammonium phosphate dryer.	The cooler off gas is collected under suction and passes through cyclones and the venturi scrubber.	There is no coater. There is no pollution control equipment on the elevators.	Sulphuric acid is not produced in this plant.

TABLE 21 AIR POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS (Cont'd)

Plant	Phosphate-Rock Grinding Mill	Phosphate Ground-Rock Storage Bin	Phosphoric Acid Reactor Vessel
CIL, Courtright*	The ball mill dust is drawn by a fan through a classifier, which returns the larger particles to the mill. The air-stream flows through two cyclones to the ground-rock storage bin.	The air is drawn from the ground-rock storage bin through a Mikro Pulseaire bag collector. The filtered air is exhausted to the atmosphere. The fines from the bag collector are returned to the bin.	The reactor is air swept to a fume scrubber containing pond water sprays, baffles, and packing rings. The scrubber is exhausted to the atmosphere and the liquid is returned to the gypsum pond system.
Simplot Chemical, Brandon	NA	NA	NA
Cominco, Trail	No grinding. The rock is purchased in a dry, finely ground state. The fine rock is conveyed pneumatically to storage silos or feed bins.	Baghouses ventilate the car dumping hopper underneath the track plus the transport air from the pneumatic conveyor. A bag-house ventilates the feed bin situated above the digester.	Ventilated gases from the reactor plus hood vent gases from the filter are scrubbed in a spray - cross-flow packed bed scrubber to remove fluorides. Reclaimed water from the NH_3 plant coolers (traces of NH_3) is the scrubbing liquid. The effluent is reused in the H_3PO_4 and $(NH_4)_2PO_4$ processes.
Western Co-op, Calgary	Ground rock is conveyed pneumatically from the grinding mill discharge fluidizer to a classifier. The coarse particles are recycled. The fines pass to a cyclone. The cyclone dust goes to the storage bins. The exhaust from the cyclone is recycled to convey more rock with a purge to a bag collector. To prevent dust losses from the grinding mill, a vent is connected to a bag collector. There is also a bag collector in the rock unloading area.	Air is drawn from the storage bins through a bag collector. This collector vents the grinding mill and dust elevator. Exhaust from the bag collector goes to the atmosphere.	The system is equipped with a spray - cross-flow packed bed scrubber to vent the reactor attack vessel, filtrate tank and seal tanks, acid seal tanks, and Lamella settler and associated tanks.
Western Co-op, Medicine Hat	All phosphate units have been shut down.		

Phosphoric Acid Filter	Phosphoric Acid Storage	Barometric Condenser	Sumps and/or Acid Splitter Boxes
The filter air is ducted to a fume scrubber containing pond water sprays, baffles, and packing rings. The liquid is returned to the gypsum pond system.	The 54% phosphoric acid storage tanks are air swept to a fume scrubber containing pond water sprays, baffles, and packing rings. The liquid is returned to the gypsum pond system.	Recycled pond water is used in the barometric condenser. The condensate is returned to the gypsum pond system.	The sumps are air swept to a fume scrubber containing pond water sprays, baffles, and packing rings. The liquid is returned to the gypsum pond system.
NA	NA	NA	NA
Vapours in the filter vacuum system are scrubbed with raw water in a Tellerette packed scrubber. The effluent is reused in the phosphoric acid and ammonium phosphate processes.	The acid storage has natural draft chimneys vented to the atmosphere.	The condenser of the vacuum evaporative slurry cooler connects to a Nash vacuum pump, which removes the noncondensables and scrubs out trace fluorides.	The floor sump is not ventilated. Neither of the two acid splitter boxes is ventilated.
The spray - cross-flow packed bed scrubber also vents the filter and the filter feed tanks.	There is no pollution control equipment on the acid storage tanks.	The spray - cross-flow packed bed scrubber also vents the barometric condenser seal tanks.	The sumps and acid splitter box are also vented to the spray - cross-flow packed bed scrubber.

TABLE 21 AIR POLLUTION CONTROL MEASURES AT PHOSPHATE FERTILIZER PLANTS (Cont'd)

Plant	Ammonium Phosphate Reactor	Ammonium Phosphate Granulator	Ammonium Phosphate Dryer
CIL, Courtright*	The reactor fumes enter the ammonia scrubber (weak phosphoric acid sprays), flow to a venturi scrubber (pond water sprays), and then go to the atmosphere. The acid is circulated to a dust scrubber and returned to the reactor. The pond water is returned to the gypsum pond system.	The granulator fumes enter the ammonia scrubber, flow to the venturi scrubber, and then go to the atmosphere. The acid is circulated to a dust scrubber and returned to the reactor. The pond water is returned to the gypsum pond system.	Dust from the dryer is fed to a cyclone. The heavier particles go to the granulator; the dust goes to the dust scrubber (weak phosphoric acid sprays). The scrubber is exhausted to the atmosphere. The acid is circulated to the ammonia scrubber and returned to the reactor.
Simplot Chemical, Brandon	Fumes and dust from the neutralizer are drawn through a venturi-type scrubber and are then discharged to the atmosphere.	Dust and fumes are drawn off the granulator by ducts through the fume scrubber (as for the neutralizer). The effluent goes back to the neutralizer.	Airflow through the dryer passes through four dust cyclones. The dust is recycled to the granulator. Air from the cyclone passes through a venturi-type liquid scrubber and then to the atmosphere.
Cominco, Trail	Ventilated fumes from the reactors, containing NH_3 and fluorides, are scrubbed by two Doyle impinger high energy scrubbers and are then discharged to the atmosphere.	There is no pollution control equipment on the blunger.	The gases from the dryer, containing fine dust, are cleaned first in cyclones followed by impinger scrubbers. The recovered dust goes back to the blunger. The scrubbing liquor flows to the blunger feed.
Western Co-op, Calgary	The gases containing ammonia, fluorides, and dust liberated from the reaction are exhausted to the fume scrubber before being discharged to the atmosphere. The scrubber liquor is recycled to the scrubber with a bleed off back to the process.	Air, ammonia fumes, fluorides, and dust from the granulator also go to the fume scrubber.	Exhaust gases and dust emissions from the dryer are drawn through cyclones followed by a wet venturi dust scrubber. The fines from the cyclone are recycled to the granulator. A scrubber bleed off goes back to the process.
Western Co-op, Medicine Hat			

* The CIL phosphate fertilizer plant ceased operations in 1986.

** Information current as of December 1985. Acid plant No. 1 will be closed and plant No. 3 (being built), which uses the double absorption process, will be brought on stream by late 1986.

Ammonium Phosphate Screens and Conveyors	Ammonium Phosphate Cooler	Ammonium Phosphate Coater, Elevators, etc.	Sulphuric Acid
The dust from the screens and conveyors enters a cyclone. The larger particles are returned to the granulator. The cyclone is exhausted into the cooler.	The dust from the cooler enters a cyclone where the large particles are returned to the granulator. The dust goes to the dust scrubber (phosphoric acid sprays).	No information available.	NA
Air and dust from the screens are drawn through four dust cyclones. The dust is recycled. The air from the cyclones goes to the atmosphere.	The air and dust from the cooler pass through four cyclones (the same equipment as for the screens).	The equipment is vented under vacuum to one of the two sets of cyclones. The air from the cyclones goes either to the atmosphere or to the scrubber.	NA
Ventilation gases from the screens contain low amounts of dust. The gas and dust are sent to the dryer exhaust system.	No cooler.	There is no coater. The emissions from elevators, transfer points, etc. are not controlled with pollution control equipment. For ventilation of bagging and bulk loading systems, cyclones and baghouses are used.	NA
The screens and elevators are vented to a cyclone followed by wet venturi dust collectors. The fines are recycled.	The product cooler is vented to a wet scrubber (Rotoclone). The collected material is recycled to the process.	There is no coater. All of the elevators are vented to cyclones followed by a wet venturi scrubber. Materials collected are recycled to the process.	Plant No. 1 uses the single absorption process, whereas plant No. 2 uses the double absorption process. Acid mist emissions from plant No. 1 are reduced by using a Brinks mist eliminator.**

TABLE 22 AIR EMISSIONS FROM PHOSPHATE FERTILIZER PLANTS

Plant	Rock Grinding	Wet Process Phosphoric Acid Plant			Ammonium Phosphate Plant				Sulphuric Acid Plant	
	Particulate (kg/d)	Fluoride (F) (kg/d)	Phosphate (P_2O_5) (kg/d)	Particulate (kg/d)	NH_3 (kg/d)	P_2O_5 (kg/d)	Particulate (kg/d)	F (kg/d)	SO_2 (kg/d)	Acid Mist (kg/d)
CIL, Courtright*	NIA	4.1	0.2	NIA	396	40	NIA	62.7	NA	NA
Cominco, Trail	NA	2.5	NIA	5	500	20	70	8.6	NA	NA
Esso Chemical, Redwater	96	8.0	1.5	100	150	4.0	300	30	1 650	Very low
Sherritt Gordon, Fort Saskatchewan	NIA	1.2	NIA	9	2 340	36	800	14	1 010	17
Simplot Chemical, Brandon	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Western Co-op, Calgary	NIA	7.7	3.0	16.3	5 918	NA	810	78	6 300	122
Western Co-op, Medicine Hat	-	-	This plant is not operating at present			-	-	-	-	-
Cominco, Kimberley	89	42	NIA	NIA	400	NIA	130	76	24 000	NIA
Belledune Fertilizer	3 000	1.55	NIA	NIA	NIA	NIA	NIA	36	NA	NA

Note: NA, not applicable; NIA, no information available
* this plant is closed

scrubbers using weak phosphoric acid and/or pond water. The weak phosphoric acid scrubbing solution is sent to the reactor and the pond water is recycled to the pond. One plant uses raw water as the scrubbing medium. Although the information received was incomplete with regard to the types of scrubbers used, the following were mentioned: spray tower, ring and cone, venturi, jet impactor cyclone, and impinger.

Upon leaving the reactor, the slurry is granulated. To accomplish this, three plants use a granulator where recycled fines provide the nuclei for the formation of granular material, three use a blunger (a tank with rotating agitators), and one uses a pug mill (horizontal shafts with paddles). Most plants treat emissions from these sources in the scrubbers used with the reactors. One of the plants with a blunger (Cominco, Trail) does not have any emission control equipment.

Emissions from dryers, coolers, screens, and transporting equipment are sent through cyclones where most of the particulates are removed. The exhaust from the cyclones is normally scrubbed with a phosphoric acid solution, with the liquor going to the reactor. Particulate removal efficiency is quite high.

After treatment, many of the scrubbed airstreams are vented to a common stack; thus, data presented are often combined emissions and emissions from individual sources, therefore, are not known.

Two plants (Cominco, Trail, and Esso Chemical, Redwater) reported emissions from the reactor and granulator as follows (average of the two plants): NH_3, 0.17 kg/t; fluoride, 0.005 kg/t; particulate, 0.047 kg per tonne of product. Emissions from the dryers, coolers, etc. for these two plants averaged the following: NH_3, 0.71 kg/t; fluoride, 0.006 kg/t; particulate, 0.133 kg per tonne of product. Using data from all plants reporting, the total emissions averaged the following: P_2O_5, 0.04 kg/t (reactor only); NH_3, 2.0 kg/t; fluoride, 0.053 kg/t; particulate, 0.46 kg per tonne of product.

8.2.3 Gypsum Pond Emissions.

General. In the production of phosphoric acid, an intermediate in the phosphate fertilizer industry, large quantities of gypsum are produced that must be disposed of. The gypsum also contains significant quantities of fluoride ion. In Europe, this waste is almost always disposed of at sea. In Canada, most plants use gypsum ponds. Most of the fluoride present precipitates; however, a significant quantity may be emitted to the atmosphere (53). Fluoride evolution from the ponds can be made negligible by raising the pH of the pond by liming (53).

Survey of Canadian plants. Six phosphate fertilizer plants are currently producing phosphoric acid as an intermediate in Canada. Four of the six plants use settling ponds. Of the remaining plants, one plant sends the waste stream to the sea, the other removes part of the fluoride present as a by-product and discharges the gypsum and remaining fluoride to a river. The smallest pond reported had a surface area of 4 ha, the largest 150 ha, with the average being 72 ha.

Fluoride emissions from gypsum ponds in the United States were found to range from 11 to 1000 kg/km^2·d, with an average value of 220 kg/km^2·d (53). Based on this emission factor, total fluoride emissions in Canada from gypsum settling ponds are estimated to be 357 t/yr.

Sulphuric acid. Six of the seven phosphate fertilizer plants in Canada use sulphuric acid as a precursor in the production of fertilizers. Three plants obtain their sulphuric acid as a by-product from a pollution control process at adjoining metallurgical complexes and the remaining three produce their own acid.

Sulphur dioxide emissions in terms of kilograms per tonne of 100% acid produced ranged from 0.92 to 26.7 kg/t, the average being 8.5 kg/t. Acid mist emissions average 0.04 kg per tonne of 100% acid produced.

9 ENVIRONMENTAL IMPACT

Elements that have a bearing on the evaluation of the potential environmental impacts of fertilizer wastewater discharges include the hazardous nature of the waste, the quantities discharged, and the receiving stream.

9.1 Wastewater Discharged from Fertilizer Plants

9.1.1 Nitrogen Fertilizer Plants. As mentioned previously, there are three types of nitrogen materials normally released in the effluent from nitrogen fertilizer plants, namely ammonia nitrogen, nitrate nitrogen, and organic nitrogen. Other minor constituents, such as trace metals, contaminants present in cooling tower and boiler blowdown, and water treatment chemicals, are also present at lower concentrations and are dependent on plant design and operation.

No biological survey data from around nitrogen fertilizer plant outfalls prior to the plant operating and during subsequent periods are available; thus, established water quality criteria are the next best thing to establish an environmental impact as higher concentrations may pose a potential hazard to aquatic life in the receiving stream or to humans or animals drinking the water.

Ammonia nitrogen. When ammonia is present in water, a chemical equilibrium exists between un-ionized ammonia, ionized ammonia, and hydroxide ions as shown in the following equation:

$$NH_3^\circ + H_2O \rightleftarrows NH_3 \cdot H_2O \rightleftarrows NH_4^+ + OH^-$$

The percentage of un-ionized ammonia in solution can be found in the literature for any given temperature and pH, e.g., the percentage un-ionized ammonia at 15 to 25°C at a pH of 7 to 8 ranges from near zero to less than 10%. The slope rises quickly when the pH is greater than 8.5.

Un-ionized ammonia (NH_3°) is the most toxic form of ammonia. The water quality criteria based on fish toxicity with a tenfold safety factor for NH_3° have been assigned the value of 0.02 mg/L (54). The ionized form of ammonia (NH_4^+) is not nearly as toxic and has been assigned the value of 1.0 mg/L (54).

Nitrate nitrogen. The toxicity of nitrate nitrogen (NO_3^--N) in water is a result of its potential conversion to nitrite, which has been shown to be highly detrimental to the bloodstream. The water quality criteria for nitrate nitrogen in domestic water supplies have been assigned the value of 10 mg/L (54).

Organic nitrogen. Most of the organic nitrogen in the effluent stream from nitrogen fertilizer plants will be urea, although amines and amides will also likely be present. No water quality criteria data for organic nitrogen are available. Using a LD_{50} value (the dose of a substance that is expected to cause death in 50% of the experimental animals) of 3000 mg/kg (55) for rabbits that have been dosed subcutaneously with urea, values of 6.75 mg/L urea or 3.17 mg/L organic nitrogen were established as the levels at which there would be no effect on the health of humans drinking 2 L of water per day (56).

9.1.2 Phosphate Fertilizer Plants. As mentioned earlier, the main contaminants discharged in effluent from phosphate fertilizer plants are fluorides, sulphates, and phosphates. The acidity of the effluent is also a concern. Other minor constituents that may be present include trace metals, radionuclides, contaminants present in cooling and boiler blowdown, and water treatment chemicals.

Fluorides. Fluorides are rare in natural surface waters, but may occur in detrimental concentrations in industrial wastewater discharges and in groundwater. Ingesting fluoride compounds can result in lowering tooth decay in children if the concentration is 0.5 to 1.0 mg of fluoride ion per litre in drinking water, mottled teeth in children if the concentration is much above 1.0 mg/L, cumulative fluorosis and skeletal effects in adults at concentrations above 3 to 4 mg/L, and death or severe symptoms (abdominal pain, diarrhea, vomiting, painful spasms of the limbs) at doses of 250 to 450 mg.

The effects of fluorides on animals are dependent upon vegetative accumulations and surface water contamination. This will lead to chronic fluoride poisoning when the water contains 10 to 15 mg/L or shorter term fluoride poisoning when the water contains 30 to 35 mg/L. Fluorides are toxic to fish at concentrations above 1.5 mg/L. Acute poisoning in animals results in stiffness, anorexia, reduced milk production, incontinence of urine and feces, weakness, and cardiac failure.

Acidity. At pH 7, hydrogen and hydroxyl ion concentrations in solution are about equal and the water is neutral. Lower pH values indicate acidity and higher values indicate alkalinity. Extremes of pH are harmful or fatal to aquatic life; humans can avoid contact when the pH is high or low. A deviation of 0.1 pH unit below 7.0 may result in eye irritation to swimmers; appreciable irritation causes severe pain. A pH below 6.0 can result in high levels of copper, iron, zinc, cadmium, and lead in drinking water because of the reaction with water lines, fixtures, etc.

Phosphorus. Increases in phosphorus in surface waters leads to a wide range of ecological disruptions, including the proliferation of nuisance water plants, accelerated eutrophication of water bodies, and bioaccumulation in and toxicity for marine fish. Proliferation of nuisance plants and eutrophication result in interference with the development of fish populations, vile stenches, danger to swimmers and boaters, contact rashes on human skin, and an improved breeding environment for flies.

Uranium and Radium 226. Radioactive materials present a host of hazards through direct exposure or by accumulation in the biological ecosystem.

"Ionizing radiation, when absorbed in living tissue in quantities substantially above that of natural background levels, is recognized as injurious. It is necessary, therefore, to prevent excessive levels of radiation from reaching any living organism: humans, fishes, and invertebrates. Beyond the obvious fact that radioactive wastes emit ionizing radiation, they are also similar in many respects to other chemical wastes. Man's senses cannot detect radiation unless it is present in massive amounts.

Radium-226 is one of the most hazardous radioisotopes of the uranium decay scheme, when present in water. The human body preferentially utilizes radium in lieu of calcium when present in food or drink. Plants and animals concentrate radium, leading to a multiplier effect up the food web.

Radium-226 decays by alpha emission into radon-222, a radioactive gas with a half-life of 3.8 days. The decay products of radon-222, in turn, are particulates that can be adsorbed onto respirable particles of dust. Radon and its decay products have been implicated in an increased incidence of lung cancer in those workers exposed to high levels (Bureau of Mines, 1971). Heating or grinding of phosphate rock would liberate radon and its decay products to the surrounding atmosphere (11)."

Radionuclides tend to accumulate in the food chain so the greatest danger is to species high in the food chain. The most significant pathway to humans is through the accumulative effects on fish and shellfish and through drinking water.

9.2 Discharge Quantities

The quantities discharged from the various plants can be determined by multiplying the wastewater discharge flow rates by the contaminant concentrations. These values are given in Tables 4 and 8.

9.3 Receiving Body of Water

Potential environmental effects are dependent upon the receiving body of water into which the plant effluent flows, such as canals, small streams, and large rivers. The receiving body flow rate is equal to the flow rate above the plant plus the volume discharged by the plant. In most cases, the flow rate from the plant can be ignored as the flow of the receiving body is very much greater.

9.4 Environmental Impact on the Receiving Body

The concentration of a given pollutant in the receiving body of water as a result of the plant wastewater discharge is compared with the minimum concentration of that pollutant determined to be hazardous (i.e., the assigned value noted above based on water quality criteria). Source severities were calculated for each plant for nitrogen discharges based on low and mean receiving body flow rates. The low flow rate represents a worst case example.

As shown in Table 23, un-ionized ammonia concentrations in the receiving water at all plants (plants from which data have been received) are lower than 0.02 mg/L - the water quality criteria assigned for un-ionized ammonia. The ionized form of ammonia concentrations in the receiving water bodies at all plants is lower than 1.0 mg/L - the water quality criteria assigned for ionized ammonia. The nitrate nitrogen and organic nitrogen concentrations in the receiving water bodies at all plants are below the 10 mg/L and 3.17 mg/L levels assigned for nitrate nitrogen and organic nitrogen respectively.

For all plants, the greatest impact occurs at the point of the wastewater discharge, where total mixing has not yet occurred. Around the outfall areas, the un-ionized and ionized ammonia concentrations could have a detrimental effect, as well as on the receiving stream below the outfall, if the ambient un-ionized and ionized ammonia concentrations are close to the assigned water quality criteria.

In addition, urea and ammonia put an oxygen demand on the river some distance downriver as ammonia and urea are oxidized by nitrifying bacteria to nitrite, nitrate, and CO_2. If the river is low in dissolved oxygen or has a low capacity to reoxygenate, toxicity to aquatic life may be caused by a lack of oxygen some distance downstream of the outfall.

Calculations are not included for fluorides, sulphate, and phosphorus because in the worst case (at Cominco, Trail, where the gypsum wastes are discharged into the Columbia River) the contaminant levels in the river as a result of the plant discharge did

TABLE 23 CALCULATED ENVIRONMENTAL IMPACT FOR PLANTS PRODUCING NITROGEN FERTILIZERS

Plant	Receiving Body Flow Rate (m^3/s)		pH of the Receiving Water Body	Source Severity							
				$NH_3°$-N		NH_4^+-N		NO_3^--N		Organic-N	
	Low	Mean		Low Receiving Body Flow Rate at pH Shown	Mean Receiving Body Flow Rate at pH Shown	Low Receiving Body Flow Rate at pH Shown	Mean Receiving Body Flow Rate at pH Shown	Low Receiving Body Flow Rate at pH Shown	Mean Receiving Body Flow Rate at pH Shown	Low Receiving Body Flow Rate at pH Show	Mean Receiving Body Flow Rate at pH Shown
CIL, Courtright	4450	4520	7.7	6.3×10^{-6}	6.2×10^{-6}	6.3×10^{-4}	6.2×10^{-4}	3.7×10^{-4}	3.7×10^{-4}	5.5×10^{-6}	5.5×10^{-6}
Cyanamid of Canada, Niagara Falls	-	-	-	-	-	-	-	-	-	-	-
Nitrochem Inc., Maitland	5660	7650	8.2	2.4×10^{-5}	1.8×10^{-5}	2.4×10^{-3}	1.8×10^{-3}	1.7×10^{-3}	1.2×10^{-3}	-	-
Canadian Fertilizer, Medicine Hat	27	88.5	-	-	-	-	-	-	-	-	-
Cominco, Calgary	14	73.8	8.2	0.001	4.7×10^{-4}	0.1	4.7×10^{-2}	4.6×10^{-2}	2.1×10^{-2}	3.6×10^{-2}	1.6×10^{-2}
Esso Chemical, Redwater	70	232	7.9	4.6×10^{-5}	4.0×10^{-6}	4.6×10^{-3}	4.2×10^{-4}	2.7×10^{-3}	2.5×10^{-4}	-	-
Sherritt Gordon, Fort Saskatchewan	73	232	8.0	1.2×10^{-3}	3.7×10^{-4}	0.12	3.6×10^{-2}	0.02	7.1×10^{-3}	0.03	8.5×10^{-3}
Simplot Chemical, Brandon	8.3	16	8.3	3.7×10^{-3}	8.7×10^{-4}	0.18	8.2×10^{-2}	9.7×10^{-2}	2.2×10^{-2}	-	-
Western Co-op, Calgary	14	73.8	8.2	1.6×10^{-4}	7.0×10^{-5}	8.0×10^{-3}	3.8×10^{-3}	9.5×10^{-3}	4.4×10^{-3}	-	-

not increase to a hazardous level, e.g., the fluoride concentration increase in the river below the Trail plant would be around 0.2 mg/L, which is much below the maximum recommended level of 1 mg/L.

As previously mentioned, approximately 4.5 t of gypsum are produced per tonne of phosphoric acid. During the chemical process, the radionuclide equilibrium that exists in the phosphate rock is disrupted, with approximately 99% of radium 226, 20 to 40% of thorium 230, and 20% of the uranium, or around 1.11 to 1.48 (^{226}Ra), 0.22 to 0.37 (^{238}U), and 0.48 to 0.66 (^{230}Th) Bq/g, being present in the gypsum.

The most significant nonoccupational impacts are associated with airborne releases of particular matter containing radionuclides and significant amounts of radon 222 from gypsum pond areas. The red bone marrow and endosteal cells of the bone receive the highest relative doses from atmospheric releases from phosphate facilities via the ingestion pathway. These emissions can be reduced substantially by covering ponds currently in use with water and inactive ponds with 1 to 2 m of clay.

The impacts associated with waterborne effluents result from water discharges associated with gypsum pond runoff to surface waters. If this effluent is double-lime treated before discharge, there should be no significant impact. Impacts on groundwater quality need to be examined.

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GLOSSARY

Aberration (chromosome): An irregularity of chromosomes that causes a duplication, a deletion, an exchange, or an alteration of the genetic material.

Acute Toxic Effect: A reaction to exposure of short-term duration that results in immediate effects that last for a short duration with little tissue reaction.

Air Stripping: Wastewater treatment process in which, as applied to nitrogen fertilizer effluents, air is passed countercurrent to a wastewater stream in a column or stripping tower to remove ammonia.

Ames Assay: A well-known short-term test that measures a chemical's ability to cause mutations in a specially engineered strain of the bacteria *Salmonella typhimurium*.

Ammoniation-Granulation: Process in which a chemical reaction with ammonia is combined with the physical process of granule formation.

Antagonism: Interaction of two or more substances such that the usual action of any one of them on living cells or tissue is altered.

Background Concentration Level: The normally occurring concentration level of a substance in a given environment and medium.

Bacteria: One-celled organisms with no chlorophyll that multiply by cell division.

Base-Pair Substitution: Gene mutation in which one base-pair in DNA (such as adenine-thymine) is replaced by another (such as guanine-cytosine).

DNA: CCA GGG CCC AAA GTG AAA -- Base-pair → CCA GAG CCC AAA GTG AAA --
GGT CCC GGG TTT CAC TTT -- Substitution GCT CTC GGG TTT CAC TTT --

CTC - specifies wrong amino acid

"The altered base sequence that results from a base-pair substitution often leads to a change in amino acid sequence in the protein that is encoded by the gene. The altered protein may function differently from the original protein, thereby causing a difference in the characteristics of the organism."

Becquerel: Unit of radioactivity equal to one disintegration per second, 3.7×10^{10} Bq = 1 Ci.

Best Practicable Technology (BPT):	The set of end-of-process industrial controls judged to perform best in the context of maximum results weighed against feasible cost.
Bioassay:	A test to determine the effect of a chemical on a living organism.
Biodegradable:	Having the ability to break down or decompose rapidly under normal environmental conditions and processes.
Biological Treatment:	Wastewater treatment process that, as applied to nitrogen fertilizer effluents, employs biological nitrification to aerobically oxidize ammonia to nitrate and biological denitrification to anaerobically reduce nitrate to nitrogen gas.
Blunger (pug mill):	U-shaped trough in which paddles mounted on twin contrarotating shafts agitate, shear, and knead a solid-liquid mixture to produce granules.
Carbon Monoxide Shift:	High- and low-temperature catalytic reaction in which steam is added to transform carbon monoxide to carbon dioxide and hydrogen in the production of synthetic ammonia.
Carcinogen(ic):	An agent capable of producing cancer in a tissue upon exposure.
Chromosome:	A form of DNA organization found in higher cells and organisms.
Chronic Exposure:	Prolonged or repeated exposure over a long-term duration.
Chronic Toxic Effect:	A reaction to exposure that results in prolonged effects characterized by pathological tissue changes for which little or ineffective repair is possible, or which continue to worsen.
Co-carcinogen:	An agent, not itself a carcinogen, that enhances the action of a given carcinogen when present in an administered mixture with that carcinogen.
Concentrated Phosphoric Acid (merchant-grade phosphoric acid):	Product of wet process phosphoric acid manufacturing, approximately 53% P_2O_5.
Cumulative (or bio-accumulative):	A toxicant tending to allow accumulation, especially within a functioning life system.
Curing:	Process by which superphosphate fertilizer material is held for a period of time ranging from a few days

to a number of weeks during which the acidulation reaction continues.

Desulphurization: Removal of hydrogen sulphide from natural gas feedstock, prior to reforming, through the use of an activated carbon or zinc oxide bed in the production of synthetic ammonia.

DNA (deoxyribonucleic acid): A large molecule that contains the genetic information responsible for cell growth and function.

Enzyme: A protein that acts as a catalyst to facilitate a specific chemical reaction to take place in a cell.

Epidemiology: The science of correlating exposure to a substance with the appearance of a specific disease or other effect in a human population group.

Estimated Permissible Concentration (EPC): The estimated level of a substance at which continuous exposure will not result in toxic effects to humans or to the ecology.

False Negative: A test result that indicates that a chemical is harmless when it is actually hazardous.

False Positive: A test result that indicates that a chemical is hazardous when it is actually harmless.

Fractionation: The process of chemically separating a complex mixture into a series of simpler mixtures (fractions).

Frameshift: One or a few base-pairs are added to the structure of DNA or deleted from it.

DNA: CCA GGG CCC GTG AAA -- Frameshift CCA GGC CCA AAG TGA AA -- GGT CCC GGG TTT CAC TTT --→ GGT CCG GGT TTC ACT TT --

Base-pair deletion
CCG GGT TTC - specify wrong amino acids
ACT - specifies no amino acid

"A frameshift mutation alters all of the genetic information after the point in the DNA at which a base-pair is added or deleted. Consequently, frameshift mutations lead to grossly altered and nonfunctional gene products."

Fugitive Emissions: Gaseous and particulate emissions that are not emitted through a primary exhaust system, such as a stack.

Genes: Units of chromosomes that determine and mediate heredity.

Genotoxins:	Chemical substances that affect genes. Used to refer to those agents reported to be oncogenic, teratogenic, or mutagenic.
Granulation:	Process in which concentrated solution is solidified by spraying it on a falling curtain or rolling bed of seed particles to build a larger particle.
Gypsum:	Calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$); by-product of the wet process reaction between phosphate rock and sulphuric acid.
Gypsum Pond:	Liquid waste receiver; primary purpose is to separate solid gypsum ($CaSO_4$) from the liquid stream that results from the production of phosphoric acid. Supernatant from the pond is used as a wet scrubbing liquor to remove fluorides from exhaust gases in ammonium phosphate production.
Hazard Assessment:	The evaluation process for determining if a substance is hazardous to humans.
High Density Prills:	Prills formed using a 99.5+% solution that lowers the number of void spaces formed to create a more dense prill.
In Vitro:	Pertains to a procedure that takes place in an artificial medium (lab equipment) without the use of live animals. Literally means "in glassware."
In Vivo:	Pertains to a biological reaction or test that occurs within the body of a live animal.
LC_{50}:	The calculated concentration of a substance in either air or water (as separate figures) that will cause the death of 50% of an experimental animal population under controlled conditions and time exposure, most often 96 hours for aquatic species. (The number 50 may or may not be a subscript.)
LD_{Lo}:	The lowest recorded dose of a substance reported to cause death in humans or animals exposed for any duration by any route other than inhalation. (Lo may or may not be a subscript.)
LD_{50}:	The lethal dose to 50% of a population; the calculated dose of a chemical substance that is expected to cause the death of 50% of an experimental animal population as determined from exposure to the substance by any route other than inhalation. (The number 50 may or may not be a subscript.)

Low Density Prill: Prills formed using a 95 to 96% solution that allows more voids in the final product, giving a less dense prill.

Metabolic Activation: The process whereby an inactive material is changed into an active material (in the context of short-term testing, this involves the conversion of a procarcinogen to a carcinogen or a promutagen to a mutagen).

Metabolism: The physical and chemical processes in an organism that transform chemicals into simpler or more complex forms.

Methanation: Catalytic reaction in which hydrogen in process gas converts trace amounts of carbon monoxide and carbon dioxide to methane and water in the production of synthetic ammonia.

Mutagenic: Resulting in a permanent change in hereditary material involving a physical change in chromosome relations, a fundamental change in the arrangement of genes, or an alteration in the makeup of DNA.

Prill: Spherical particle formed by the solidification of a solution droplet.

Prilling: Process in which concentrated solution is solidified by spraying it in a tower so that the drops formed fall countercurrent to a stream of cooling air.

Primary Reformer: Set of catalyst-filled tubes in which natural gas (methane) reacts with steam to form carbon monoxide and hydrogen in the production of synthetic ammonia.

Representative Plant: Typical plant defined to establish a base upon which to evaluate the emissions of the industry. The plant has average industry parameters.

Salmonella-Microsome Test: This test was developed by Dr. Bruce Ames, a biochemist at the University of California in the early 1970s. The test measures the mutagenic potential to produce genetic changes of a chemical.

In the Ames test, bacteria and the chemical are put together in a petri dish and incubated. If the chemical(s) being tested is a mutagen, it will mutate the bacteria, which would be difficult to detect. Thus, reverse mutation is used. Ames and his colleagues have developed bacteria that already

have mutations in the genes that govern the ability to make histidine, which allows growth.

If the chemical being tested is a mutagen and if it acts on the bacteria, the already mutated bacteria are mutated again. As a result, the bacteria make histidine and begin to grow. The colonies are visible after 48 hours.

Currently, five strains are normally employed in the test: TA 98, TA 100, TA 1535, TA 1537, and TA 1538. Strains TA 98, TA 1537, and TA 1538 carry frameshift mutations and, therefore, are reverted by agents that will produce new frameshifts. Strains TA 100 and TA 1535 carry missense mutations and are reverted by agents that cause base-pair substitutions, although it has been observed that strain TA 100 will also respond to some frameshift mutations.

In 1975, it was shown that 90% of the known carcinogens tested were mutagenic in the Ames test. This high correlation was made possible by the discovery that many carcinogens are not active as such but are metabolized to the active form by enzymes in the liver and other organs. This mammalian metabolic system could be duplicated in the microbial mutagenicity assays by incorporating into the test system an extract from the liver of a rat (S9). The liver enzymes converted the carcinogens to their active forms, which were detected as mutagens by the bacteria.

S9 (liver homogenates):

For general mutagenesis screening, liver homogenates from rats induced with a polychlorinated biphenyl (PCB) mixture (Aroclor 1254) are used. Other tissues have been used; however, rat liver is the most convenient source of activating enzymes. It is essential for efficient detection of a wide variety of carcinogens requiring metabolic activation. It has been found that liver from Aroclor-induced rats is the most efficient for detecting different classes of carcinogens.

Secondary Reformer:

Catalytic reactor in which compressed air is mixed with process gas from the primary reformer to produce a synthesis gas with a hydrogen-to-nitrogen mole ratio of 3:1 in the production of synthetic ammonia.

Steam Stripping:	Process in which process condensate flows down a column countercurrent to steam, which extracts ammonia and methanol from the condensate.
Synergism:	The ability of a substance to achieve or cause an appreciably different or greater effect than its own usual effect when present in conjunction with another substance.
Teratogenic:	Inducing structural and/or functional deviation in an embryo during its development, resulting in congenital birth defects.
Toxicity:	The ability of a chemical molecule or compound to produce injury once it reaches a susceptible site in or on the body.
Toxicology:	Study of the action, detection, and treatment of poison and poisonings.
Urea Hydrolysis:	Process in which urea in condensate is converted through a series of intermediate products back to ammonia and carbon dioxide, which are then driven off with steam.

APPENDIX A

PROVINCIAL EFFLUENT GUIDELINES AND STANDARDS FOR THE FERTILIZER INDUSTRY

TABLE A1 EFFLUENT LIMITATIONS FOR SELECTED POLLUTANTS FROM SELECTED CHEMICAL INDUSTRIES - AIR

Industry	Parameter	Limitation in Given Jurisdiction: Alberta	British Columbia*	Ontario (concentration at point of impingement - 0.5 hour average)		Manitoba
Fertilizer and related: Sulphuric acid	SO_2	2 kg per tonne of 100% acid produced 3 kg/t, 24 hour average 0.20 ppm $_v$-maximum cumulative 0.5 hour calculated ground level concentration	A-1.5 kg per tonne of 100% acid B-6 kg per tonne of 100% acid	Carbon monoxide	6000 $\mu g/m^3$ air	Ammonia emissions from the plant shall not exceed 3 ppm by volume averaged over 1 hour periods in a residential area except during power failures, breakdowns, etc.
				Chlorine	300 $\mu g/m^3$ air	
				Chlorine dioxide	85 $\mu g/m^3$ air	
				Fluorides (total)	8.6 $\mu g/m^3$ air as HF, Apr. 15 - Oct. 15	
					17.2 $\mu g/m^3$ air as HF, Oct. 16 - Apr. 14	Nitrogen oxides (as NO_2)
	$SO_3 + H_2SO_4$ mist	0.075 kg/t, 24 hour average	SO_3: A-25 mg/m^3 B-50 mg/m^3	Hydrocarbons	No collective limit	Not to exceed 6 kg/t of 100% acid
				Hydrogen chloride	100 $\mu g/m^3$ air	
				Mercury (total)	5.0 $\mu g/m^3$ air	An opacity of 10% (may exceed 10% up to 1 hour during power failures, upsets, etc.)
				Nitrogen oxides	500 $\mu g/m^3$ air as NO_2	
Nitric acid	Nitrogen oxides (as NO_2)	New plants: 1.5 kg per tonne of 100% acid produced, design 2.25 kg/t, 24 hour average 2.75 kg/t, 0.5 hour average Existing plants: 3.5 kg per tonne of 100% acid produced, design 5 kg/t, 24 hour average 6 kg/t, 0.5 hour average 0.17 ppm, maximum average 1 hour calculated ground level concentration	A-2.5 kg per tonne of 100% acid B-10 kg per tonne of 100% acid	Particulates (suspended)	100 $\mu g/m^3$ air	Solids from any process shall not be released in excess of 0.23 grams per standard cubic metre at the point of emission
				Sulphur dioxide	830 $\mu g/m^3$ air	
				Sulphuric acid	100 $\mu g/m^3$ air	
Phosphate fertilizer	Fluoride	Phosphoric acid plants: 0.0125 kg per tonne of P_2O_5 daily average, soluble, as HF Ammonium phosphate plants: New: 0.015 kg per tonne of product daily average Existing: 0.025 kg/t, daily average, as HF 5.0 ppb_v	A-0.10 kg/t, total, as SiF_4 4.3 mg/m^3 (6.4 ppm) as HF B-0.15 kg/t, total, as SiF_4 4.3 mg/m^3 (6.4 ppm) as HF			

Note: The Cominco, Trail, plant comes under the *Pollution Control Objectives for the Mining, Smelting and Related Industries of British Columbia, 1979*. The emission objective for the ammonium phosphate fertilizer plant in this complex is fluoride as HF - 0.05 to 0.15 kg per tonne of P_2O_5.

* Level A will be required for all new operations. Existing plants must meet level B within the shortest time technically feasible.

TABLE A2 EFFLUENT LIMITATIONS FOR SELECTED POLLUTANTS FROM SELECTED CHEMICAL INDUSTRIES - WATER

Industry	Parameter	Limitation in Given Jurisdiction		
		Alberta	British Columbia*	Ontario
Fertilizer and related	Suspended solids	25 mg/L	Marine and fresh waters: A,B - 20 mg/L	15 ppm_w
	Cyanide	0.025 mg/L	A,B - 0.10 mg/L	
	pH	6.5 to 9.5	Marine water: A - 6.5 to 8.5 B - 6.5 to 9.0 Fresh water: A,B - 6.5 to 8.5	5.5 to 9.5
	Nitrogen: Ammonia	35 mg/L Ammonia plants: Existing (2728 L/t of NH_3) 0.095 kg/454 kg daily average 0.191 kg/454 kg, not to be exceeded during any 1-day period grab sample: 0.286 kg/454 kg daily max. New (1227 L/t of NH_3) 0.048 kg/454 kg daily average 0.095 kg/454 kg, not to be exceeded during any 1-day period grab sample: 0.143 kg/454 kg daily max.	Marine and fresh waters: A - 10 mg/L (as N) B - 15 mg/L (as N)	10 mg/L (as N)
	Nitrate	20 mg/L	Marine and fresh waters: A - 10 mg/L B - 50 mg/L	
	Organic	10 mg/L	Marine and fresh waters: A - 15 mg/L (kjeldahl) B - 25 mg/L (kjeldahl)	
	Phosphate	5 mg/L	Fresh water: A - 1.0 mg/L B - 10 mg/L	1.0 mg/L
	Metals: Chromium	0.30 mg/L (hexavalent)	0.2 mg/L (total)	1.0 mg/L
	Lead	0.10 mg/L	0.2 mg/L	1.0 mg/L
	Mercury	0.0005 mg/L	Marine and fresh waters: A - 0.002 mg/L B - 0.050 mg/L	0.001 mg/L (essentially 0)
	Nickel	1.0 mg/L	0.2 mg/L	1.0 mg/L
	Zinc	1.0 mg/L	Marine water: A,B - 0.2 mg/L Fresh water: A,B - 0.2 mg/L	1.0 mg/L
	Toxicity	24 hour static LC_{50}, 50% effluent	96 hour LC_{50}:** Marine water: A - 50%; B - 45% Fresh water: A - 100%; B - 90%	

* Level A will be required for all new operations. Existing plants must meet level B within the shortest time technically feasible.

** Concentration of effluent in which 50% of test organisms remain alive for a 96 hour period, e.g., marine water, B level = 45%, i.e., in a solution composed of 45% effluent and 55% make-up water, 50% must remain alive for the 96 hour test period. For A level, the same must be achieved in a stronger mixture, composed of 50% effluent.

Note: The following limits apply to the one fertilizer plant in Manitoba. (Summary of an order of the Clean Environment Commission under the Clean Environment Act: Manitoba to Simplot Chemical Ltd.)

1) The Applicant shall, with regard to the discharge of liquid effluent on and after the 16th day of May, 1985, and thereafter between the 16th day of May of any year and the 14th day of September of the same year, not direct any discharge of liquid effluent from the said operation into the river.

2) The Applicant shall carry out the irrigation of soil with liquid effluent in accordance with the following limits, terms, and conditions:

   a) the pH of the said liquid effluent shall not be lower than 6.0 nor higher than 9.0;
   b) the application rate of nitrogen to the soil shall not exceed 225 kg of nitrogen per hectare per year;
   c) the nitrate-nitrogen (NO_3-N) contained in the top 120 cm of soil, sampled from any area directly affected by the Applicant's irrigation program of that same year, as indicated by soil samples taken within 8 months of the close of the irrigation season during which irrigation was carried out and subjected to analysis in accordance with Appendix B to this order, shall not be in excess of 265 kg of nitrogen per hectare;
   d) the said liquid effluent shall be applied only to land where crops are actively growing;
   e) there shall be no application of liquid effluent to land from the 1st day of October of any year to the 15th day of May of the following year.

3) The Applicant shall direct all surface runoff and process wastewater leaving the plant site area for disposal via the effluent ditches toward the river or toward the irrigation storage ponds through the main effluent monitoring station.

4) The Applicant shall ensure that all existing and new effluent ditches and new holding ponds are lined with a continuous and impervious liner of a quality acceptable to the said Division.

5) The Applicant shall not discharge effluent toward the river:

   a) subject to Clause 1, where the quality of the effluent, as sampled at the main monitoring station, contains contaminants in excess of any of the following limits during the dates described in the following table:

Contaminant	Limits in a 24 hour period (kg)	
	On and before September 14, 1985	On and after September 15, 1985
Total Nitrogen as N	204.0	204.0
Total Ammonia Nitrogen as N	135.0	91.0
Total Phosphorus as P	20.0	20.0
Sulphates as SO_4	2722.0	2722.0

As determined from analysis of a 24 hour composite sample of the effluent by taking into account the total volume of effluent so discharged during the said 24 hour period

   b) where the pH of the effluent is less than 6.0 or more than 9.0 at any time;
   c) where the total chlorine residual of the effluent is in excess of 1.4 mg/L;
   d) where there is physical evidence of oil or grease in the effluent.

APPENDIX B

MONITORING AND EFFLUENT CONTROL MEASURES USED AT NITROGEN AND PHOSPHATE FERTILIZER PLANTS

Nitrogen Fertilizer Industry

In Appendix Tables B1 to B3, the plants are represented by letters as follows:

Canadian Industries Limited	as	A
Cyanamid of Canada	as	B
Nitrochem	as	C
Canadian Fertilizer	as	D
Cominco, Calgary	as	E
Cominco, Carseland	as	F
Cominco, Trail	as	G
Esso Chemical	as	H
Sherritt Gordon	as	I
Simplot Chemical	as	J
Western Co-op, Calgary	as	K
Western Co-op, Medicine Hat	as	L

All tables are compiled from 1978 questionnaire survey data.

Phosphate Fertilizer Industry

In Appendix Tables B4 to B8, the plants are represented by letters as follows:

Canadian Industries Limited	as	A
Cominco, Trail	as	G
Esso Chemical	as	H
Sherritt Gordon	as	I
Simplot Chemical	as	J
Western Co-op, Calgary	as	K
Western Co-op, Medicine Hat	as	L
Cominco, Kimberley	as	M
International Minerals and Chemical Corporation Ltd.	as	N
Belledune Fertilizer	as	O

All tables are compiled from 1978 questionnaire survey data.

TABLE B1 MONITORING AND RECORDING FOR NITROGEN PLANTS

	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H	Plant I	Plant J	Plant K	Plant L
Final effluent monitoring	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes(5)
Frequency and method of sampling	Chemical(1) parameter 24 hour composite flow and temperature daily	Continuous 24 hour composite	-	All effluent is sampled continuously from one stream	24 hour composite	Automatic sampler	Daily composite	Automatic sampler	Sampled continuously 24 hour (4) composite	Daily continuous proportional sampler	-	One grab sample per month
Type of record kept	Continuous analysis charts are maintained 3 to 4 weeks; others indefinitely	Analysis of daily 24 hour composite samples	See note (2)	Daily with monthly and yearly reports	Daily total (3)	Weekly	Plant records	Monthly report	See note (4)	Daily analysis record (6)	-	Monthly
Name of the regulatory agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	-	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency

Note:
(1) continuous analysis
(2) flow indicator record and record of the daily analysis of the flow proportional samples for ammonia, ammonium nitrate, urea, chromate, and pH
(3) NH_3-N, NO_3-N, organic nitrogen, total suspended solids all as lb/d
(4) for a 24 hour composite sample analysis for NH_3-N, NO_3-N, organic nitrogen, PO_4, suspended solids, Cr^{+6}, Ni, Cu, pH; total flow is measured by a weir
(5) final effluent goes to gypsum pond; springs in area are sampled periodically
(6) analyzed for NH_3-N, total nitrogen, P, Na, SO_4, pH, Mg, Ca, conductivity, total chlorine residual, and flow; each 32 ha of irrigated land is also sampled and monitored for pH, NO_3-N, P, K, Na, Ca, Mg, conductivity, and bulk density

TABLE B2 MISCELLANEOUS IN-PLANT CONTROL INFORMATION

	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H	Plant I	Plant J	Plant K	Plant L
Stream could be sampled:												
a) Ammonia Plant:												
Cooling tower blowdown	No tower	X	-	X	-	X	-	-	-	X	-	X
Compressor blowdown	X	X	-	X	-	X	-	-	-	X	X	X
Boiler blowdown	X	X	-	X	-	X	-	-	-	X	X	X
Process effluent	X	X	-	X	X	X	-	X	X	X	-	-
b) Ammonium Nitrate Plant:												
Process effluent*	X	X	X	-	X	-	-	X	-	X**	-	-
c) Urea Plant:												
Cooling tower blowdown	-	-	-	X	-	X	-	-	-	X	-	-
Compressor blowdown	X	-	X	X	-	-	-	-	-	X	-	-
Boiler blowdown	-	-	-	X	-	-	-	-	-	-	-	-
Process effluent	X	-	X	X	X	X	-	X	-	X**	-	-
Recovers chemicals	Yes	Yes	500 t of NH_3	No	No	No	-	-	-	NH_4NO_3, urea, and NH_3	No	No
Measures taken to lower water consumption	-	No	Yes, complete recycle	No	No	Yes, recycle	Yes, cooling tower recycle	Yes, cooling tower recycle	Yes, holding pond to collect contaminated water for recycle	Yes, process effluent used in products	Planned	Yes

Note: only plant I reported that ammonium sulphate plant process stream could be sampled
* no other data available
** no effluent to sewer

TABLE B3 EXTERNAL CONTROL MEASURES

	Plant A	Plant B	Plant C	Plant D	Plant E	Plant F	Plant G	Plant H	Plant I	Plant J	Plant K	Plant L
pH control of wastewater	Yes	No	No	Yes	No	No	No	No	No	Yes	Yes	Not required
pH control limits	6.5 to 8.5	-	-	6.5 to 8.5	-	-	-	6.5 to 9.5	-	6.0 to 9.0	6.5 to 9.5	-
Chemicals used	H_2SO_4	-	-	1) H_2SO_4 2) NaOH	-	-	-	None	-	H_2SO_4 CO_2 NaOH	H_2SO_4	-
Annual consumption of chemical (kg)	Nil	-	-	1) 36 300 2) 25 400	-	-	-	-	-	As required	2000	-
Flow measuring devices on plant effluent	No, because of large volume of once-through cooling water	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes	No
Suspended solids	-	Settling pond	Settling pond	Settling pond	-	-	-	Settling pond	-	-	Settling pond	-
Oil removal	For NH_3 and urea plants, oil from process stream or spent lubrication oil is collected in drums and burned in powerhouse or by waste disposal firm	Skimmer for oil from NH_3 and urea plants	Oil skimmer for final effluent from the complex	Belt separation	-	-	-	-	-	Oil separators installed for compressor blowdown. Oil is recovered as fuel for boilers.	Flotation for final effluent from the complex	-
Chromate removal	-	-	-	-	-	-	-	-	-	Chromate system replaced several years ago.	Not necessary due to installation of low-chromate addition system	Low chromate water treatment
Physico-chemical and biological treatment	Ion exchange ammonia plant	-	Steam stripping for NH_3 and urea plant condensate	Steam stripping for ammonia and urea plants. Ion exchange for urea plant.	-	-	-	-	-	Nitrogen-rich streams are stored in ponds over winter and used to irrigate agricultural land during summer	-	-

pH Control

Out of 10 plants, only four (A, J, K, N) have pH control of wastewater. Plants O and H monitor only pH, whereas plant M has pH controls for some streams. Plants I, G, and L do not have any controls. Only five plants reported pH control limits, chemicals used, and annual consumption of chemicals (except plants A and J).

Plant	pH Control Limits	Chemicals Used	Annual Consumption
A	6.5-8.6	H_2SO_4	Nil
N	6.5-9.5	Quicklime	8140 t
M	6.5-7.5	Lime	590 t
K	6.5-9.5	H_2SO_4	1 t
J*	6.0-9.0	H_2SO_4, CO_2, and NaOH	As needed

* Plant J monitors the pH of its combined effluent at its main monitoring station and adjusts the pH of the streams back at the plant if the monitored pH falls outside the range.

Flow Measuring Devices

Only five plants (H, I, J, K, M) have flow measuring devices. Plant G has plans for flow measuring devices.

TABLE B4 MONITORING AND RECORDING FOR PHOSPHATE FERTILIZER PLANTS

Information	Plant A	Plant G	Plant H	Plant I	Plant K	Plant L	Plant M	Plant N	Plant O
Monitor the final effluent	Yes	Yes	Yes	Yes	Yes	Flows to gypsum pond. Springs in the area are sampled.	Yes	Yes	Yes
Frequency and method of sampling	Continuous 24 hour composite sample		Continuous 24 hour composite sample	Continuous 24 hour composite sample	Daily continuous			Grab and 24 hour composite	Automatic
Type of effluent record kept	Phosphorus as P_2O_5, fluoride, ammonia, nitrate, urea, pH, flow, and temperature (flow and pH are measured daily; temperature is measured weekly)	Full	Daily flow rate, NH_3-N, NO_3-N, organic nitrogen, PO_4, total suspended solids, and pH	NH_3-N, NO_3-N, organic nitrogen, PO_4, suspended solids, Cr^{+6}, Ni, Cu, and pH; total flow is measured by a weir	Daily flow rate, Cr^{+6}, P_2O_5, F, total dissolved solids, N (NO_3, NH_3), and pH	Monthly	Flow, pH, charts and bio-assay reports	Sulphuric acid plant - cooling water daily grab for pH and then composited weekly for suspended solids and SO_4. Phosphoric acid plant - cooler water daily grab for pH, composited weekly for suspended solids, F, and P_2O_5. Neutralization plant discharge records same as for phosphoric acid plant.	pH, P_2O_5, and fluorine content
Name of regulatory agency advised by the plant	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	Provincial agency	No

TABLE B5 MISCELLANEOUS IN-PLANT CONTROL INFORMATION

	Stream could be sampled separately																
	Cooling tower blowdown from plants		Gypsum slurry from plants						Boiler blowdown from plants			Process effluent from plants					
	N	O	A	N	M	K	L	I	O	M	K	O	A	N	G	M	I
Ammonium phosphate			X										X		X		
Phosphoric acid	X		X	X	X	X	X	X				X	X		X	X	
Sulphuric acid	X								X		X				X	X	
Other										X*				X**			X***

* from steam plant
** from normal and triple superphosphate plants
*** from ammonium sulphate plant

Chemical Recovery

Nine plants reported recovering chemicals. Three plants (A, G, and N) recovered chemicals as indicated below. Plants O, H, I, M, K, and L did not report recovering any chemicals.

Plant A: Hydrofluosilicic acid, 4200 t/yr
Plant G: Hydrofluosilicic acid, 900 t/yr; fluoride 653 t/yr
Plant N: Hydrofluosilicic acid, 455 000 t/yr

Measures Taken to Lower Water Consumption

Seven plants reported that they have taken measures to lower water consumption by recycling. Plant O did not take any measures. Plant A did not specify anything. A common method of reducing water consumption is to recycle cooling water through cooling towers, which results in cooling tower blowdown discharges only.

TABLE B6 GYPSUM DISPOSAL

	Plant A	Plant G	Plant H	Plant I	Plant K	Plant L	Plant M	Plant N	Plant O
How gypsum is disposed of	Pond	-	Pond	Pond	Pond	Pond	Pond	Diked disposal	Water body
Disposal period	12 yr	-	10 yr	Since 1965	Since 1965	Since 1956	Since 1968	Since 1961	10+ yr
How many more years it can be disposed of	Indefinitely	-	10 yr	As long as possible	20 yr	30 yr	50 yr	30-40 yr	Indefinitely
Study for alternative gypsum disposal	No	Yes*	Yes**	No	No	No	No	No	Yes*
Gypsum pond water recycled	Yes, contaminated water recycle	No	Yes, contaminated water recycle	Yes, contaminated water recycle	Yes, clear water recycle	Yes, clear water recycle	Yes, clear water recycle	Yes, contaminated water recycle	No
Percentages of gypsum pond water flow recycled to plants	H_3PO_4 plant, 99%; $(NH_4)_2PO_4$ plant, 1%	NA	As indicated in this report	H_3PO_4 plant and $(NH_4)_2PO_4$ plant	$NH_4H_2PO_4$ plant, 1%; H_3PO_4 plant, 99%	H_3PO_4 plant, 100% (estimated)	H_3PO_4 plant, 100%	Normal and triple superphosphate plant, 19%; $(NH_4)_2PO_4$ plant, 80%; H_3PO_4 plant, 1%	NA

Note: plant J effluent is combined with nitrogen plant effluent
* information available
** confidential data, not available

TABLE B7 TESTING METHODS USED BY NITROGEN FERTILIZER PLANTS

Contaminant	Testing Method	Plants Using Method
Ammonia	Specific ion electrode	B, L, A
	Indophenol blue (autoanalyzer)	A
	Diphenyl carbazide	C
	Titration	J, F, K
	Colourimetric standard methods 1975 No. 418B	G
Chromate	Material balance	B
	Naquadat 24101L	I, L
	Standard methods 1975 No. 307A	G
	Atomic absorption	D
	Spectrophotometer	K
	No measurement	A, C, E, F
Phosphate	Amino napthtyl sulphonic acid	A
	Colourimetric	I, K, J
	Naquadat 15420L	F
	Standard methods 1975 No. 425E	I, H
	Stannous chloride/gravimetric quinoline	L, J
	APHA 223	D
	No measurement	C, E
Sulphate	Thorin indicator	A
	Barium sulphate turbidity	B, J
	Barium chloride titration	J, F
	Gravimetric	L
	Standard methods 1975 No. 425E	G
	No measurement	C, I, E, K
Sulphite	No measurement	None
Zinc	Atomic absorption	F, D
Nitrate	Specific ion electrode	A, B, I, J, K, L, E
	Formaldehyde	C
	Standard methods 1975 No. 419B	H, L
	APHA No. 419D	G, L, D
Urea	Colourimetric	A, B, C
	No measurement	D, F, I, H, K, L, E
	Titration	J
CO_2	Van Slyke	J
	Titration	F
Monoethanolamine	Material balance	B
	Titration	D, F, J
Biochemical oxygen demand	Electrode	A
	APHA No. 219	D
Chemical oxygen demand	Dichromate method	A
	APHA No. 220	D
Oil and grease	Ether extract	A
	Carbon tetrachloride extract	F, J
	APHA No. 137	D
Suspended solids	Filtration	A, B, J, E, K
	Standard methods 1975 No. 208D	H
	Standard methods 1975 No. 208C	L
	Naquadat 10401L	I
	APHA No. 148	D
	No measurement	C
pH	pH meter	A, B, J, E, K
	Titration	C
	Naquadat 10301L	I, L
	Standard methods 1975 No. 424	H
	APHA No. 144	D

TABLE B8 TESTING METHODS USED BY PHOSPHATE FERTILIZER PLANTS

Contaminant	Testing Method	Plants Using Method
Chromate	AOAC 1970	O
	Naquadat 24101L	I, L
	Standard methods 1975 No. 307A	H
	Atomic absorption spectrophotometry	K
Sulphate	Thorin indicator	A
	Gravimetric	G, M, N
	Standard methods 1975 No. 307A	H
Phosphate	AOAC 2.023 (c), 2.024, 2.025(b)	O
	Ammonia sulphonic acid	A
	Photometric	N
	Naquadat 15420L	I
	Standard methods 1975 No. 425E	H, L
	Molybdate	G, M
	Colourimetric	K
Fluoride	Specific ion electrode	O, A, G, M, N, K, L
	Standard methods 1975 No. 414B	H
Ammonia	AOAC 2.049, 2.050, 2.051	O
	Idophenol blue (autoanalyzer)	B
	Kjeldahl distillation	I
	Specific ion electrode	L
	Nessler's reagent	G
	Titration	M
Dissolved solids	Gravimetric	A, K
	Naquadat 10307L	I
	Filtration, evaporation	M
	Standard methods 1975 No. 308C	L
Suspended solids	Millipore filter	A, M
	Gravimetric	N, G, K
	Naquadat 10407L	I
	Standard methods 1975 No. 208D	H
	Standard methods 1975 No. 208E	L
pH	Potentiometric	O
	pH meter	M
	Electrode	G

APPENDIX C

SCREENING SURVEY AT FERTILIZER PLANTS

Screening Survey

No.	Description	Date
B1	Belledune Fertilizer, final effluent	Nov. 10-11, 1980
B2	Belledune Fertilizer, final effluent	Nov. 11-12, 1980
B3	Belledune Fertilizer, freshwater intake	Nov. 10-11, 1980
B4	Belledune Fertilizer, saltwater intake	Nov. 10-11, 1980
G1	Nitrochem, final outfall	Nov. 17-18, 1980
G2	Nitrochem, final outfall	Nov. 18-19, 1980
G3	Nitrochem, ditch water	Nov. 18-19, 1980
G4	Nitrochem, intake water	Nov. 18-19, 1980
G5	Nitrochem, final outfall	Nov. 19-20, 1980
W1	Western Co-op, Calgary, final effluent	Dec. 9-10, 1981
W2	Western Co-op, Calgary, gypsum sewer	Dec. 9-10, 1981
W3	Western Co-op, Calgary, intake water	Dec. 10-11, 1981
W4	Western Co-op, Calgary, final effluent	Dec. 10-11, 1981
W5	Western Co-op, Calgary, final effluent	Dec. 11-12, 1981
E1	Esso Chemical, industrial sewer	Jan. 5-6, 1981
E2	Esso Chemical, industrial sewer	Jan. 6-7, 1981
E3	Esso Chemical, industrial sewer	Jan. 7-8, 1981
E4	Esso Chemical, clear water sewer	Jan. 6-7, 1981
E5	Esso Chemical, intake water	Jan. 6-7, 1981
C1	Cominco, Trail, final effluent	Jan. 18-19, 1981
C2	Cominco, Trail, final effluent	Jan. 19-20, 1981
C3	Cominco, Trail, final effluent	Jan. 20-21, 1981
C4	Cominco, Trail, intake water after water treatment	Jan. 19-20, 1981
C5	Cominco, Trail, gypsum sewer	Jan. 20-21, 1981

TABLE C1 SCREENING SURVEY AT FERTILIZER PLANTS, CONVENTIONAL PARAMETERS (1980/1981 data)

	B1	B2	B3	B4	G1	G2	G3	G4	G5	W1	W2
pH	3.0	3.0	6.8	7.0	9.7	9.4	9.5	4.0	9.5	8.7	1.56
Temperature	-	-	-	-	4°C	10°C	7.5°C	-	18.5°C	15.6°C	15.6°C
Total Solids	36 000	30 700	45	22 800	-	-	-	-	-	-	-
Total Dissolved Solids	-	-	-	-	-	-	-	-	-	1 560	20 100
Suspended Solids	6 300	9 700	5*	6	-	-	-	-	-	3	48
Volatile Suspended Solids	-	-	-	-	-	-	-	-	-	2	13
Hardness	4 022	6 900	30	4 432	-	-	-	-	-	415	4 500
Total Alkalinity	-	-	-	-	-	-	-	-	-	159	-
Biochemical Oxygen Demand	-	-	-	-	-	-	-	-	-	-	-
Chemical Oxygen Demand	-	-	-	-	-	-	-	-	-	-	-
Total Organic Carbon	4.0	6.0	6.0	2.0	-	-	-	-	-	-	-
Inorganic Carbon as C	-	-	-	-	-	-	-	-	-	34	<1
Organic Carbon as C	-	-	-	-	-	-	-	-	-	9	16
Ammonia Nitrogen as N	0.8	2.5	0.14*	0.14*	690	710	610	11	720	26	380
Total Kjeldahl Nitrogen	-	2.2	0.6	0.5	-	-	-	-	29	29	480
NO_3 Nitrogen as N	0.03	0.03	0.12	0.13	190	220	230	3	190	31	370
Nitrite Nitrogen as N	0.005	0.005	0.005*	0.005*	0	0.9	1.8	0	1.0	0.72	1.3
Total Phosphate as P	56	-	0.21	0.12	<0.1	<0.1	<0.1	0.2	0.6	3.5	5 000
Orthophosphate as P	41	-	0.01	0.13	-	-	-	-	-	3.1	3 500
Sulphate (SO_4)	4 100	4 300	9.5	3 700	370	370	120	20	280	325	4 300
Chloride (Cl)	-	-	-	-	86	87	640	28	100	340	-
Fluoride (F)	240	380	0.25*	0.7	-	-	-	0.16	0.51	1.6	-

Note: all values in mg/L, except pH and temperature; data of 1984/1985 analysis are summarized in Tables 4 and 8.
* less than detectable limit
** total suspended solids

W3	W4	W5	E1	E2	E3	E4	E5	C1	C2	C3	C4	C5
7.8	8.34	8.6	8.6	7.8	7.7	7.0	8.1	-	-	-	-	-
21°C	16.7°C	16.7°C	25.6°C	25.6°C	25.6°C	25.6°C	0.6°C	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-
250	1 470	1 716	3 320	7 214	3 345	253	225	2 900	2 780	2 800	90	6 200
17	7	9	20	27	18	3	11	760**	750**	920**	5**	7 000**
3	3	4	12	16	11	1	11	-	-	-	-	-
194	431	499	307	285	267	122	170	-	-	-	-	-
153	179	195	640	414	780	36	140	-	-	-	-	-
-	-	-	-	-	-	-	-	5	7	2	2*	5
-	-	-	-	-	-	-	-	125	75	50	30	780
-	-	-	-	-	-	-	-	2	14	12	2	18
34	39	39	83	103	4	31	-	-	-	-	-	-
4	10	8	32	43	5	6	-	-	-	-	-	-
1.2	61	69	580	1 000	500	6.6	0.22	20	11.5	10.5	0.012	3.2
1.3	63	73	580	1 000	500	6.6	0.31	23	12	12	<0.1	<0.1
0.65	65	70	350	770	420	1.6	0.28	0.165	0.167	0.160	0.150	0.107
<0.01	1.2	1.5	2.0	3.4	4.2	0.07	0.04	0.016	0.014	0.018	0.005*	0.037
1.3	3.5	3.8	2.2	2.9	1.7	14.0	0.15	37.3	39.2	59.0	0.0069	370
1.1	3.4	3.3	1.5	1.7	1.1	12.5	0.10	-	-	-	-	-
39	320	300	1 040	850	630	84	44	1 650	1 370	1 560	13.1	2 100
7.6	350	510	13	12	22	3.4	2.9	1.87	0.99	1.49	0.73	0.5*
1.3	1.4	1.3	0.56	0.53	0.45	5.1	0.15	0.05*	0.05*	0.05*	0.09	0.05*

TABLE C2 SCREENING SURVEY AT FERTILIZER PLANTS, METALS (1984/1985 data)

	B1	B2	B3	B4	G1	G2	G3	G4	G5	W1	W2	W3
Arsenic	0.60	0.43	0.05*	0.19	<0.005 µg/L	<0.005 µg/L	<0.005 µg/L	<0.005 µg/L	<0.005 µg/L	-	-	-
Antimony	0.1*	0.1*	0.1*	0.1*	<0.002	<0.002	<0.002	<0.002	<0.002	-	-	-
Aluminum	-	-	-	-	-	-	-	-	-	-	-	-
Barium	-	-	-	-	-	-	-	-	-	-	-	-
Beryllium	0.01*	0.01*	0.01*	0.01*	<0.002	<0.002	<0.002	<0.002	<0.002	-	-	-
Calcium	-	-	-	-	-	-	-	-	-	-	-	-
Magnesium	-	-	-	-	-	-	-	-	-	-	-	-
Sodium	-	-	-	-	-	-	-	-	-	-	-	-
Cadmium	0.07	0.06	0.01*	0.07	<0.003	<0.003	<0.003	<0.003	<0.003	0.003	0.007	<0.002
Cobalt	-	-	-	-	-	-	-	-	-	-	-	-
Chromium	0.15	0.20	0.03	0.01	0.90	0.82	0.33	<0.01	1.20	0.33	27	<0.05
Copper	0.03	0.04	0.01*	0.01*	0.05	0.04	0.09	0.01	0.04	0.02	7.5	<0.02
Cyanide (Total)	0.02*	0.02*	0.02*	0.02*	-	-	-	-	-	<0.05	<0.05	<0.05
Mercury	0.066	0.057	0.00040	0.0017	<0.002	<0.002	<0.002	<0.002	<0.002	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L
Manganese	-	-	-	-	-	-	-	-	-	0.04	4.3	0.02
Molybdenum	-	-	-	-	-	-	-	-	-	-	-	-
Nickel	0.07	0.07	0.01*	0.01	0.02	0.01	0.01	<0.01	<0.01	<0.03	3.2	<0.03
Phosphorus	-	-	-	-	-	-	-	-	-	-	-	-
Lead	0.20	0.22	0.02*	0.04	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.4	0.01
Selenium	0.35	0.41	0.05*	0.05	<0.005	<0.005	<0.005	<0.005	<0.005	-	-	-
Tin	-	-	-	-	0.037	0.037	0.035	0.011	0.035	-	-	-
Strontium	-	-	-	-	0.09	0.06	0.12	0.11	0.05	-	-	-
Titanium	-	-	-	-	-	-	-	-	-	-	-	-
Vanadium	-	-	-	-	0.635	0.408	0.106	0.002	1.38	-	-	-
Zinc	0.31	0.19	0.01*	0.38	0.19	0.23	0.08	0.02	0.15	0.1	20	0.02
Iron	6.90	5.69	0.04	0.07	-	-	-	-	-	-	-	-
Silicon	-	-	-	-	-	-	-	-	-	-	-	-
Thallium	0.1*	0.1*	0.1*	0.1	0.025	0.025	0.032	0.018	0.024	-	-	-
Silver	0.02*	0.02*	0.02*	0.02*	<0.002	<0.002	<0.002	<0.002	<0.002	-	-	-

Note: all values in mg/L unless indicated otherwise
data reported by Environment Canada Wastewater Technology Centre laboratory in Burlington in parentheses
-, no metals detected
* less than detectable limit

W4	W5	E1	E2	E3	E4	E5	C1	C2	C3	C4	C5
-	-	(<0.005)	(<0.005)	(<0.005)	(<0.005)	(<0.005)	0.15* (<0.005)	0.15* (<0.005)	0.15* (<0.005)	0.15* (<0.005)	0.62 (<0.005)
-	-	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	0.08* (<0.01)	0.08* (<0.01)	0.08* (<0.01)	0.08* (<0.01)	0.32* (<0.01)
-	-	(1.7)	(0.48)	(0.48)	(0.36)	(0.18)	9.1	7.8	6.2	0.09*	102
-	-	-	-	-	-	-	1.02	2.02	1.53	0.0218	5.63
-	-	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(<0.001)	(0.010)	(0.014)	(0.012)	(0.003)	(3.2)
-	-	-	-	-	-	-	798	1 650	1 440	22	20 100
-	-	-	-	-	-	-	5.57	5.59	6.25	4.92	22.7
-	-	-	-	-	-	-	37.7	25.7	25.8	1.44	2.68
<0.002	0.02	<0.002 (<0.003)	<0.002 (<0.003)	<0.002 (<0.003)	<0.002 (<0.003)	<0.002 (<0.003)	0.01* (<0.016)	0.01* (<0.01)	0.01* (<0.009)	0.01* (<0.003)	0.04* (<1.5)
-	-	-	-	-	-	-	0.015*	0.015*	0.015*	0.015*	0.06*
0.32	0.22	4.1 (4.5)	4.5 (4.2)	4.6 (4.6)	0.10 (0.07)	<0.05 (<0.01)	0.516 (1.0)	0.461 (<0.56)	0.4 (0.42)	0.015* (<0.01)	7.45 50
<0.02	<0.02	<0.02 (0.02)	<0.02 (0.01)	<0.02 (0.01)	<0.02 (0.01)	<0.02 (0.01)	0.045 (0.18)	0.05 (0.07)	0.035 (0.05)	0.084 (0.08)	0.45 9.0
<0.05	<0.05	<0.05	<0.005	<0.05	<0.005	<0.05	-	-	-	-	-
<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	<0.2 µg/L	1.49 µg/L	0.99 µg/L	0.95 µg/L	0.2* µg/L	9.36 µg/L
0.04	0.04	0.02 (0.03)	0.03 (0.02)	0.02 (0.01)	0.08 (0.05)	0.02 (0.0)	0.0274	0.0328	0.0463	0.003*	0.50
-	-	-	-	-	-	-	0.15*	0.15*	0.15*	0.15*	0.6*
<0.03	<0.03	0.03 (<0.01)	<0.03 (<0.01)	<0.03 (<0.01)	<0.03 (<0.01)	<0.03 (<0.01)	0.08* (0.16)	0.08* (0.03)	0.08* (0.03)	0.08* (0.06)	0.41 (5.0)
-	-	-	-	-	-	-	34.4	50.0	78.8	0.3*	111
0.03	0.03	0.068 (0.04)	0.064 (<0.01)	0.051 (<0.01)	0.007 (<0.01)	0.007 (<0.01)	0.084 (0.05)	0.08* (0.03)	0.08* (<0.03)	0.08* (<0.01)	0.320 (<0.5)
-	-	<0.003	0.003	<0.003	<0.003	<0.003	0.15* (<0.005)	0.15* (<0.005)	0.15* (<0.005)	0.15* (<0.005)	0.6* (<0.005)
-	-	(0.058)	(0.060)	(0.060)	(0.021)	(0.025)	0.2* (0.14)	0.2* (0.047)	0.2* (0.077)	0.2* (0.004)	0.8* (22)
-	-	(0.08)	(0.08)	(0.09)	(0.01)	(0.16)	1.2 (1.0)	2.0 (0.52)	1.66 (0.30)	0.119 (0.06)	21.3 (50)
-	-	-	-	-	-	-	0.0808	0.0757	0.058	0.0085*	0.47
-	-	(0.14)	(0.07)	(0.06)	(0.011)	(0.004)	0.05 (0.28)	0.05* (0.14)	0.05* (0.17)	0.05* (0.03)	0.36 (64)
0.10	-	0.31 (0.63)	0.35 (0.25)	0.31 (0.23)	0.05 (0.02)	0.01 (0.01)	0.128 (0.35)	0.169 (0.17)	0.147 (0.13)	0.02* (0.03)	3.28 (21)
	-	-	-	-	-	-	5.82	14.6	11.4	0.038	206
-	-	-	-	-	-	-	42.7	30.6	22.4	1.91	236
-	-	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)	(<0.01)
-	-	(0.020)	(0.020)	(0.019)	(0.016)	(0.018)	(0.68)	(0.30)	(0.21)	(0.006)	(38)

TABLE C3 SCREENING SURVEY AT FERTILIZER PLANTS, ORGANIC CONTAMINANTS, BASE NEUTRAL GROUP (1984/1985 data)

	B1	B2	B3	B4	G1	G2	G3	G4	G5	W1	W2
Polynuclear Aromatics											
Acenaphthylene	-	-	-	-	2	T	-	-	-	-	-
Anthracene	-	-	-	-	T	-	-	-	-	-	-
Fluoranthene	-	-	T	-	-	T	T	T	-	-	-
Fluorene	-	-	-	-	-	-	-	-	-	-	-
Naphthalene	T	-	-	-	-	T	-	-	-	-	-
Pyrene	-	-	-	-	T	-	-	-	-	-	-
1,2-Dichlorobenzene	-	-	-	-	T	-	-	-	-	-	-
1,3-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-
Nitrosamines											
N-nitrosodimethylamine	-	-	-	-	-	-	-	-	2	-	-
Phthalate Esters											
Butyl Benzylphthalate	-	-	T	-	-	-	-	-	-	T	-
Di-n-butylphthalate	2	T	1	5	3	4	2	3	-	T	T
Diethylphthalate	-	T	T	-	T	-	T	-	-	T	T
Dimethylphthalate	-	-	-	T	-	-	-	-	T	-	-
Di-n-octylphthalate	-	-	12	-	T	-	T	-	-	T	-
Bis (2 ethylhexyl) phthalate	3	2	71	75	3	2	2	-	-	0-10	1-10
Haloethers											
Bis (2 chloroethyl) ether	T	-	T	-	T	-	-	-	-	-	-
Bis (2 chloroisopropyl) ether	T	T	T	-	T	T	T	T	-	-	-
Other Compounds											
2,4-Dinitrotoluene	-	-	-	T	-	-	-	-	-	-	-
1,2-Diphenylhydrazine	Present	-	Present	-	-	-	-	-	-	-	-
Isophorone	Present	-	Present	-	Present	Present	-	-	-	-	-

Note: All values in mg/L.
-, not detected; T, trace amount.
The following compounds were tested but were not detected in any sample:
Polynuclear Aromatics: Acenaphthene, Benzo(a) anthracene, Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(ghi) perylene, Benzo(a) pyrene, Chrysene, Dibenzo(ah) anthracene, Ideno(1-2c-d) pyrene.
Nitrosamines: N-nitrosodiphenylamine, N-nitroso-di-n-propylamine.
Haloethers: 4-Bromophenyl phenyl ether, Bis (2 chloro etoxy) methane.
Other compounds: 2-Chloronaphthalene, 3,3'-dichlorobenzidine, 2,6-Dionitrotoluene, Hexachlorobutadine, Hexachlorocyclopentadiene, Hexachloroethane, Nitrobenzene.

W3	W4	W5	E1	E2	E3	E4	E5	C1	C2	C3	C4	C5
-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	T	-	-	-	-
-	-	T	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	T
-	-	-	-	T	-	-	-	T	T	T	T	T
-	-	T	-	-	-	-	-	T	T	1-10	-	T
-	-	-	-	-	-	-	-	-	-	-	-	T
-	T	T	T	-	-	-	-	-	-	-	-	T
-	-	-	-	-	-	-	-	2	1-10	-	-	-
-	T	-	-	-	-	-	-	T	17	40	-	92
T	T	0-10	T	T	T	T	T	T	T	11	1-10	1-10
-	T	T	-	-	-	-	-	T	T	T	-	T
-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	T	T	T	T	-	-	14	T	T	1-10	-
0-10	1-10	1-10	-	1-10	1-10	0-10	1-10	135	1-10	17	30	1-10
-	-	-	-	-	-	-	-	-	T	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-	-

TABLE C4 SCREENING SURVEY AT FERTILIZER PLANTS, VOLATILE PRIORITY POLLUTANTS (1984/1985 data)

Compound (µg/L)	Screening Survey								
	G4	G5	W1	W3	W5	C1	C2	C4	C5
Dichloromethane	230	236	103	17	80	5	2	1	31
Acetone-NPP	P	P	P	P	P	P	P	P	P
Trichlorofluoromethane or 1,1-Dichloroethylene	-	-	-	-	-	-	-	-	T
1,1-Dichloroethane	-	-	-	-	-	-	-	-	-
Trans-1,2-Dichloroethylene	1	-	-	-	-	-	-	-	-
Chloroform	171	189	20	-	31	37	37	51	134
1,2-Dichloroethane	-	-	-	-	-	-	-	-	-
1,1,1-Trichloroethane	-	-	-	-	-	-	-	-	-
Carbon Tetrachloride	-	-	-	-	-	-	-	-	-
Bromodichloromethane	-	8	-	-	4	125	130	120	-
1,2-Dichloropropene	5	2	5	4	-	-	3	-	-
Trans-1,2-Dichloropropene	-	-	-	-	8	8	5	5	9
Trichloroethylene or Cis 1,3-Dichloropropane	T	2	1	1	1	-	1	T	2
1,1,2-Trichloroethane or Dibromochloromethane or Benzene	T	-	-	-	-	2	1	1	4
Bromoform	-	-	-	-	-	T	1	-	10
1,1,2,2-Tetrachloroethane	-	-	-	-	-	4	2	-	10
Tetrachloroethylene	-	-	-	-	-	13	T	-	150
Toluene	-	T	-	-	-	8	10	-	T
Chlorobenzene	-	-	-	-	-	-	-	-	-
Ethylbenzene	-	-	-	-	-	-	-	-	-

Note: -, not detected
P, present - could not be quantified
T, trace - normally less than 1 µg/L

TABLE C5 SCREENING SURVEY AT FERTILIZER PLANTS, ORGANIC CONTAMINANTS, ACID GROUP (1984/1985 data)

Compound (µg/L)	Screening Survey							
	B1	B2	G1	G2	G3	G4	G5	W5
2,4-Dimethylphenol	-	T	-	-	-	-	T	-
2-Chlorophenol	-	-	T	-	-	-	-	-
p-chloro-m-cresol	-	-	-	-	T	-	-	-
2,4-Dinitrophenol	-	-	-	-	1	-	-	-
2-Nitrophenol	-	-	-	-	T	-	-	-
4-Nitrophenol	-	-	-	-	T	-	-	-
Pentachlorophenol	-	-	-	-	-	-	4	T
Phenol	T	1	12	3	1	T	20	-

Note: -, not detected; T, trace.
Toluene was detected in trace amounts in samples W2, E2, C1, and C2. None of the acid group compounds were detected in samples W1, W3, W4, C3, C4, C5, E1, E2, E3, E4, and E5. Other acid group compounds, such as 2,4-Dichlorophenol and 4,6-Dinitro-o-cresol, were not detected in any samples.

TABLE C6 SCREENING SURVEY AT FERTILIZER PLANTS, ORGANIC CONTAMINANTS, PURGABLE GROUP (1984/1985 data)

Compound (µg/L)	Screening Survey			
	B1	B2	B3	B4
Benzene	-	127	-	6
Chlorobenzene	6	5	T	T
Chloroethane	T	-	67 mg/L	T
Chloroform	T	T	1	T
Chloromethane	T	468	-	1
Dichlorodifluoromethane	T	T	T	T
1,2-Dichloroethane	T	1	-	-
Trans-1,2-Dichloroethylene	T	-	-	-
Ethylbenzene	-	1	-	T
Dichloromethane	3 mg/L	2 mg/L	153	106
1,1,2,2 Tetrachloroethane	-	-	-	T
1,1,2,2 Tetrachloroethene	3	1	T	-
Toluene	-	32	4	3
Trichlorofluoromethane	T	2	-	-

Note: -, not detected; T, trace.
Other compounds, such as Bromodichloromethane; Bromoform; Bromomethane; Carbon Tetrachloride; 2-chloroethylvinylether; bis-chloromethylether; Dibromochloromethane; 1,1-Dichloroethane; 1,1-Dichloroethylene; 1,2-Dichloropropane; 1,3-Dichloropropane; 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; Trichloroethylene; and vinyl chloride, were not detected in any samples. None of the purgable group compounds were detected in the samples from Nitrochem, Western Co-op, Esso Chemical, or Cominco.

TABLE C7 SCREENING SURVEY AT FERTILIZER PLANTS, ORGANIC CONTAMINANTS, PESTICIDE GROUP

Compound (µg/L)	Screening Survey		
	W2	W3	E5
Aldrin	T	-	-
4,4'-DDT	T	-	-
Alpha-Endosulfan	-	1	-
Endrin	-	-	T
Heptachlor	T	-	-
4,4' DDE	T	-	-

Note: -, not detected; T, trace.
Other pesticides, such as alpha-BHC; beta-BHC; gamma-BHC; delta-BHC; chlordane; 4,4'-DDD; beta-Endosulfan; Endosulfan sulphate; Heptachlor Epoxide; PCBs; Toxaphene; and Dieldrin, were not detected in any samples. None of the pesticide group compounds were detected in the samples from Belledune Fertilizer, Nitrochem, Cominco, Esso Chemical, or Western Co-op (except as stated above).

TABLE C8 SCREENING SURVEY AT FERTILIZER PLANTS, RADIOCHEMICAL ANALYSIS

Screening Survey		^{226}Ra (Bq/L)	U (mg/L)
Western Co-op, final effluent	Dec. 10-11, 1980	0.74	0.01
Esso Chemical, industrial sewer	Jan. 5-6, 1981	0.04	-
Esso Chemical, intake water	Jan. 6-7, 1981	0.63	-
Esso Chemical, clean water	Jan. 6-7, 1981	0.22	-
Esso Chemical, industrial sewer	Jan. 6-7, 1981	0.48	-

APPENDIX D

EFFLUENT CHARACTERISTICS OF UNTREATED COOLING WATER, COMPRESSOR AND BOILER BLOWDOWN, AND SCRUBBER SOLUTIONS

Nitrogen Fertilizer Industry

In Appendix Tables D1 and D2, the plants are represented by letters as follows:

Canadian Industries Limited	as	A
Cyanamid of Canada	as	B
Nitrochem	as	C
Canadian Fertilizer	as	D
Cominco, Calgary	as	E
Cominco, Carseland	as	F
Cominco, Trail	as	G
Esso Chemical	as	H
Sherritt Gordon	as	I
Simplot Chemical	as	J
Western Co-op, Calgary	as	K
Western Co-op, Medicine Hat	as	L

All tables are compiled from 1978 questionnaire survey data.

TABLE D1 EFFLUENT CHARACTERISTICS OF UNTREATED COOLING WATER AND COMPRESSOR AND BOILER BLOWDOWN DURING NORMAL PLANT OPERATIONS

	Ammonia Plant			Urea Plant			Total for the Complex		
Parameter	D	E	J	D	E	J	D	E	J
Typical Flow (m^3/d)	3 168	113 625	93	950	22 125	10	4 118	149 985	988 (includes utilities)
Ammonia-N (mg/L)	1.35 (70; yearly)	-	2.0 (20; yearly)	1.35 (70; yearly)	- (500; monthly)	-	1.35 (70; yearly)	243 (500; monthly)	50 (200; four times per year)
Chromate (mg/L)	0	-	0	0	-	-	0	-	-
Phosphate (mg/L)	0.9 (2; monthly)	-	0	0.9 (2; monthly)	-	-	0.9 (2; monthly)	-	10
Sulphate (mg/L)	912 (1 100; twice per week)	-	320	912 (1 100; twice per week)	-	-	912 (1 100; twice per week)	-	1 500 (2 000; four times per year)
Sulphite (mg/L)	0	-	0	0	-	-	0	-	-
Zn (mg/L)	0.6 (1.4; yearly)	-	0	0.6 (1.4; yearly)	-	-	0.6 (1.4; yearly)	-	-
Oil and Grease (mg/L)	1.5 (5; yearly)	-	2	1.5 (5; yearly)	-	-	1.5 (5; yearly)	-	<1*
Suspended Solids (mg/L)	8 (15; monthly)	-	-	8 (15; monthly)	-	-	8 (15; monthly)	29 (200; monthly)	10
NO_3-N (mg/L)	-	-	-	-	-	-	-	52 (200; monthly)	25 (100; yearly)
pH before Treatment	7.8 (7.0-8.5; weekly)	-	7.4	7.0 (7.0-8.5; weekly)	-	6.5	7.8 (7.0-8.5; weekly)	7.5	7.4
pH after Treatment	8.5 (6.5-9.5; weekly)	-	7.5	8.5 (6.5-9.5; weekly)	-	-	8.5 (6.5-9.5; weekly)	-	7.5

Note: Values are typical. Maximum concentration and potential frequency of maximum concentration in parentheses.

* Data collected after treatment. All other data, except pH after treatment, collected before treatment.

TABLE D2 PROCESS EFFLUENT (SCRUBBER SOLUTIONS AND CONDENSER WATER) DURING NORMAL PLANT OPERATIONS

	Ammonium Plant				Urea Plant		Ammonium Nitrate Plant	
	Plant A		Plant D		Plant D		Plant A	
Major Contaminants	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment	Before Treatment	After Treatment
Ammonia (mg/L)	700	0.5(20; eight times per day)	750 (900; four times per year)	20 (50; six times per year)	25 000 (45 000; four times per year)	20(620; four times per year)	10 (100; three times per year)	5 (10; twice per week)
Nitrate (mg/L)	Nil	-	0	0	0	0	0.1 (100; three times per year)	600 (800; three times per week)
Sulphate (mg/L)	-	-	0	0	0	0	-	-
Urea (mg/L)	Nil	-	0	0	500 (25 000; twice per year)	20(210; four times per year)	Nil	-
CO_2 (mg/L)	-	-	3 290 (3 500; four times per year)	0	0	0	-	800 (1 000; three times per week)
Mono-ethanolamine (mg/L)	Nil	-	0	0	0	0	Nil	-
Oil (mg/L)	Nil	-	0	0	0	0	-	-
pH	-	4(2-8; daily)	7.5	9.2	0	-	-	-
Flow (m^3/d)	1 440	-	3 900	-	650	-	2 700	-

Note: Values are typical. Maximum concentration and potential frequency of maximum concentration in parentheses.

APPENDIX E

RESULTS OF BIOLOGICAL TESTING OF FERTILIZER PLANT FINAL EFFLUENT FOR GENOTOXIC ACTIVITY

TABLE E1 BELLEDUNE FERTILIZER, *Salmonella* MUTAGENICITY TEST ON STRAIGHT EFFLUENT

Final Dilution of Straight Effluent	Equivalent Original Effluent Volume (mL)**	Tester Strain (Number of Histidine Positive Revertants per Plate)*									
		TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:2	0.5	10	13	134	123	16	9	9	15	38	30
1:4	0.25	11	14	137	126	14	10	11	11	41	29
1:8	0.12	8	12	116	109	13	8	11	7	33	36
1:16	0.06	10	13	122	117	10	13	13	15	31	30
1:32	0.03	9	13	132	140	11	9	9	12	36	37
Negative Control	PBS***	8	16	133	134	10	9	11	9	36	33
Positive Control											
NaAz	5 µg/plate	1334	-	1446	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1435	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	1734	-	1385	-
B(a)P	10 µg/plate	-	-	147	979	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture
*** phosphate buffered saline

TABLE E2 NITROCHEM, *Salmonella* MUTAGENICITY TEST ON STRAIGHT EFFLUENT

Final Dilution of Straight Effluent	Equivalent Original Effluent Volume (mL)**	Tester Strain (Number of Histidine Positive Revertants per Plate)*									
		TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:2	0.5	18	20	97	122	8	11	10	12	16	38
1:4	0.25	14	18	128	125	7	13	13	13	35	32
1:8	0.12	20	15	88	105	12	12	11	15	39	30
1:16	0.06	16	17	130	130	12	10	11	14	51	ND
1:32	0.03	13	16	131	149	17	10	7	11	39	34
Negative Control	PBS***	14	17	118	129	11	13	10	13	45	34
Positive Control											
NaAz	5 µg/plate	1290	-	1137	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1072	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	800	-	1434	-
B(a)P	10 µg/plate	-	-	147	723	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture; ND, not detected
* mean value of colony counts from triplicate plates
** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture
*** phosphate buffered saline

TABLE E3 WESTERN CO-OP, *Salmonella* MUTAGENICITY TEST ON STRAIGHT EFFLUENT

Final Dilution of Straight Effluent	Equivalent Original Effluent Volume (mL)**	Tester Strain (Number of Histidine Positive Revertants per Plate)*									
		TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:2	0.5	11	15	81	81	17	18	12	11	28	23
1:4	0.25	16	15	76	93	15	18	13	13	27	25
1:8	0.12	16	18	61	81	17	12	11	14	27	26
1:16	0.06	13	16	81	95	15	17	10	17	32	ND
1:32	0.03	14	18	98	101	13	15	10	16	37	29
Negative Control	PBS***	9	15	83	82	14	17	15	17	25	28
Positive Control											
NaAz	5 µg/plate	809	-	1337	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1128	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	1121	-	965	-
B(a)P	10 µg/plate	-	-	98	583	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture; ND, not detected
* mean value of colony counts from triplicate plates
** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture
*** phosphate buffered saline

TABLE E4 ESSO CHEMICAL, *Salmonella* MUTAGENICITY TEST ON STRAIGHT EFFLUENT

Final Dilution of Straight Effluent	Equivalent Original Effluent Volume (mL)**	Tester Strain (Number of Histidine Positive Revertants per Plate)*									
		TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:2	0.5	5	8	80	79	-	-	8	17	28	25
1:4	0.25	6	7	72	79	-	-	10	10	22	26
1:8	0.12	11	9	69	78	-	-	15	12	22	20
1:16	0.06	7	8	72	72	-	-	11	13	26	19
1:32	0.03	8	9	72	73	-	-	11	12	24	19
Negative Control	PBS***	5	6	62	69	-	-	13	13	25	18
Positive Control											
NaAz	5 µg/plate	1207	-	1257	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	924	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	800	-	747	-
B(a)P	10 µg/plate	-	-	102	636	-	-		-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture
*** phosphate buffered saline

TABLE E5 COMINCO, *Salmonella* MUTAGENICITY TEST ON STRAIGHT EFFLUENT

Final Dilution of Straight Effluent	Equivalent Original Effluent Volume (mL)**	Tester Strain (Number of Histidine Positive Revertants per Plate)* TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:2	0.5	10	6	71	70	13	11	5	7	23	24
1:4	0.25	9	6	63	73	10	8	7	6	28	20
1:8	0.12	8	12	54	66	12	7	6	7	25	18
1:16	0.06	7	8	72	67	9	10	4	7	25	30
1:32	0.03	7	9	68	70	9	7	9	9	32	25
Negative Control	PBS***	8	8	60	62	8	8	10	8	30	23
Positive Control											
NaAz	5 µg/plate	892	-	1483	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	648	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	1004	-	490	-
B(a)P	10 µg/plate	-	-	96	1123	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture
*** phosphate buffered saline

TABLE E6 BELLEDUNE FERTILIZER, *Salmonella* MUTAGENICITY TEST ON EXTRACT

Final Dilution of Extract**	Equivalent Original Effluent Volume (mL)***	Tester Strain (Number of Histidine Positive Revertants per Plate)* TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:25	10	14	14	192	159	24	17	18	29	40	77
1:40	6.2	13	13	236	236	26	20	14	31	36	55
1:80	3.1	14	19	227	243	12	20	11	29	31	45
1:160	1.6	12	19	197	203	8	19	11	19	33	44
1:320	0.8	11	22	147	157	10	21	8	18	33	44
1:640	0.4	12	18	144	125	13	14	8	26	24	42
1:1280	0.2	12	21	127	133	11	18	8	21	19	46
Solvent Control	DMSO**	12	20	119	136	9	14	9	14	23	38
Positive Control											
NaAz	5 µg/plate	1272	-	1402	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1584	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	754	-	608	-
B(a)P	10 µg/plate	-	-	128	1075	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** final concentration of solvent in plate is 4% dimethyl sulphoxide (DMSO)
*** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture

TABLE E7 NITROCHEM, *Salmonella* MUTAGENICITY TEST ON EXTRACT

Final Dilution of Extract**	Equivalent Original Effluent Volume (mL)***	Tester Strain (Number of Histidine Positive Revertants per Plate)* TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:25	10	15	16	218	174	22	19	25	17	87	75
1:40	6.2	16	12	184	176	21	18	21	17	57	53
1:80	3.1	12	17	165	164	15	18	17	16	41	40
1:160	1.6	11	14	166	171	16	17	15	10	48	41
1:320	0.8	13	16	157	160	16	10	13	15	38	36
1:640	0.4	13	12	150	154	15	12	13	13	35	42
1:1280	0.2	10	10	144	156	16	10	15	13	36	38
Solvent Control	DMSO**	11	11	159	157	11	15	13	15	43	35
Positive Control											
NaAz	5 µg/plate	1118	-	1059	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	730	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	619	-	552	-
B(a)P	10 µg/plate	-	-	144	733	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** final concentration of solvent in plate is 4% dimethyl sulphoxide (DMSO)
*** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture

TABLE E8 WESTERN CO-OP, *Salmonella* MUTAGENICITY TEST ON EXTRACT

Final Dilution of Extract**	Equivalent Original Effluent Volume (mL)***	Tester Strain (Number of Histidine Positive Revertants per Plate)* TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:25	10	3	17	181	173	16	13	21	28	88	69
1:40	6.2	11	19	188	163	17	13	16	28	54	58
1:80	3.1	11	20	102	167	16	16	17	28	47	65
1:160	1.6	ND	18	126	122	18	15	16	28	26	46
1:320	0.8	6	17	129	128	12	11	19	22	35	37
1:640	0.4	8	12	72	146	13	12	16	22	27	38
1:1280	0.2	10	22	84	121	12	17	9	25	25	49
Solvent Control	DMSO**	13	17	90	134	15	15	16	25	32	39
Positive Control											
NaAz	5 µg/plate	1251	-	1299	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	809	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	726	-	754	-
B(a)P	10 µg/plate	-	-	120	793	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture; ND, not detected
* mean value of colony counts from triplicate plates
** final concentration of solvent in plate is 4% dimethyl sulphoxide (DMSO)
*** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture

TABLE E9 ESSO CHEMICAL, *Salmonella* MUTAGENICITY TEST ON EXTRACT

Final Dilution of Extract**	Equivalent Original Effluent Volume (mL)***	Tester Strain (Number of Histidine Positive Revertants per Plate)*									
		TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:25	10	16	18	203	175	19	12	19	28	52	76
1:40	6.2	16	15	165	160	14	17	20	24	40	55
1:80	3.1	13	12	140	149	12	17	20	28	31	40
1:160	1.6	14	11	132	114	10	21	15	23	32	47
1:320	0.8	15	14	131	113	11	16	14	25	31	46
1:640	0.4	12	11	105	124	10	18	10	20	25	25
1:1280	0.2	14	13	114	121	10	19	15	29	29	36
Solvent Control	DMSO**	13	11	119	128	11	19	13	26	26	32
Positive Control											
NaAz	5 µg/plate	1145	-	1181	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	906	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	652	-	689	-
B(a)P	10 µg/plate	-	-	115	618	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** final concentration of solvent in plate is 4% dimethyl sulphoxide (DMSO)
*** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture

TABLE E10 COMINCO, *Salmonella* MUTAGENICITY TEST ON EXTRACT

Final Dilution of Extract**	Equivalent Original Effluent Volume (mL)***	Tester Strain (Number of Histidine Positive Revertants per Plate)*									
		TA1335		TA100		TA1537		TA1538		TA98	
			+S9		+S9		+S9		+S9		+S9
1:25	10	14	15	130	156	12	12	14	17	26	26
1:40	6.2	10	15	160	155	8	16	14	18	34	41
1:80	3.1	12	14	156	164	9	12	6	19	45	40
1:160	1.6	14	17	152	131	8	12	11	18	39	29
1:320	0.8	13	10	137	131	13	11	13	15	32	37
1:640	0.4	13	15	150	145	6	10	8	17	35	39
1:1280	0.2	14	10	157	141	9	12	12	17	36	36
Solvent Control	DMSO**	10	13	142	145	10	12	9	17	33	30
Positive Control											
NaAz	5 µg/plate	1035	-	1211	-	-	-	-	-	-	-
9-AA	100 µg/plate	-	-	-	-	1141	-	-	-	-	-
2NF	5 µg/plate	-	-	-	-	-	-	688	-	703	-
B(a)P	10 µg/plate	-	-	151	1017	-	-	-	-	-	-

Note: S9 is a metabolic activation mixture
* mean value of colony counts from triplicate plates
** final concentration of solvent in plate is 4% dimethyl sulphoxide (DMSO)
*** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture

TABLE E11 CHROMOSOME ABERRATIONS IN CHINESE HAMSTER CELLS FOLLOWING EXPOSURE TO EXTRACTS OF EFFLUENT*

Final Dilution of Extract	Dimethyl Sulphoxide (DMSO) Concentration in Diluted Extract (%)	Equivalent Original Effluent Volume (mL)	Plant (Percentage Metaphase Plates with Chromosome Aberrations)**									
			Belledune Fertilizer		Nitrochem		Western Co-op		Esso Chemical		Cominco	
				+S9		+S9		+S9		+S9		+S9
1:10	10	25	T	29.8	41.7***	22.2***	1.0	1.0	2.0	1.0	4.0	0.0
1:20	5	12.5	10.9	1.0	4.0	5.0	1.0	0.0	3.0	0.0	1.0	0.0
1:40	2.5	6.2	0.0	0.0	0.0	0.0	0.0	-	0.0	-	0.0	-
1:80	1.2	3.1	0.0	-	-	-	-	-	-	-	-	-
1:160	1.2	1.6	-	-	-	-	-	-	-	-	-	-
1:320	1.2	0.8	-	-	-	-	-	-	-	-	-	-
1:640	1.2	0.4	-	-	-	-	-	-	-	-	-	-
1:1280	1.2	0.2	-	-	-	-	-	-	-	-	-	-
Solvent Control (DMSO)												
1:10 Dilution			1.0	2.0	1.0	2.0	1.0	0.0	0.0	0.0	0.0	0.0
1:20 Dilution			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1:40 Dilution			0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1:80 Dilution			0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0
Control (Aflatoxin B_1)												
10^{-5} M			-	-	-	-	-	-	-	-	-	-
5×10^{-6} M			0.0	57.9	0.0	57.9	0.07	2.2	0.0	63.3	0.0	63.3

Note: -, not analyzed
* 3 hour exposure to effluent extract
** a minimum of 100 metaphase plates are scored unless the number is limited as a result of mitotic inhibition
*** mitotic inhibition, <1 metaphase in 4000 cells

TABLE E12 DNA REPAIR TEST ON EXTRACTS OF INDUSTRIAL EFFLUENTS (UNSCHEDULED DNA SYNTHESIS IN CULTURED HUMAN FIBROBLASTS)

Final Dilution of Extract	Dimethyl Sulphoxide (DMSO) Concentration in Diluted Extract (%)	Equivalent Original Effluent Volume (mL)**	Plant (Average Number of Grains per Nucleus)*									
			Belledune Fertilizer		Nitrochem		Western Co-op		Esso Chemical		Cominco	
				+S9		+S9		+S9		+S9		+S9
1:10	10	25	0	0	0	0	0	0	0	0	0	T
1:20	5	12.5	0	0	0	0	0	0	0	1	0	1
1:40	2.5	6.2	0	0	0	0	0	0	1	0	0	0
1:80	1.2	3.1	0	0	0	0	0	0	0	0	1	0
1:160	1.2	1.6	0	0	0	0	0	0	0	0	1	0
1:320	1.2	0.8	0	1	0	0	1	0	0	0	0	0
1:640	1.2	0.4	0	0	0	1	1	0	0	0	0	0
1:1280	1.2	0.2	0	0	0	0	1	0	0	0	1	0
Solvent Control (DMSO)												
0	10		0	0	0	0	0	0	0	0	1	0
0	5		0	0	0	0	0	0	0	0	0	0
0	2.5		0	0	0	0	0	0	0	0	0	1
0	1.2		0	0	0	0	1	0	0	0	0	0
Control (Aflatoxin B_1)												
10^{-4} M			1	40	1	40	0	31	0	31	1	42
10^{-5} M			0	21	0	21	0	27	0	27	0	25

Note: T, toxic effects; i.e., cells changed morphology and/or detached from cover glass
* minimum of 30 nuclei scored, unless otherwise stated
** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture

TABLE E13 DNA REPAIR INHIBITION TEST ON EXTRACTS OF INDUSTRIAL EFFLUENTS (EFFECT ON UN-INDUCED UNSCHEDULED DNA SYNTHESIS IN CULTURED HUMAN FIBROBLASTS)

Final Dilution of Extract	Dimethyl Sulphoxide (DMSO) Concentration in Diluted Extract (%)	Equivalent Original Effluent Volume (mL)**	Plant (Average Number of Grains per Nucleus)*									
			Belledune Fertilizer		Nitrochem		Western Co-op		Esso Chemical		Cominco	
				+S9		+S9		+S9		+S9		+S9
1:10	10	25	0	0	2	37	0	0	30	T	29	T
1:20	5	12.5	0	31	42	37	46	39	49	47	37	48
1:40	2.5	6.2	41	37	45	41	48	33	51	50	ND	46
1:80	1.2	3.1	38	40	45	44	50	39	48	52	25	47
1:160	1.2	1.6	40	42	51	45	52	36	49	52	32	47
1:320	1.2	0.8	42	40	52	-	52	40	50	-	41	-
1:640	1.2	0.4	40	40	55	-	52	36	51	-	45	-
1:1280	1.2	0.2	43	40	54	-	-	39	52	-	48	-
Solvent Control (DMSO)												
1:10	10		28	25	28	25	30	44	30	44	39	38
1:20	5		44	48	44	48	46	44	46	44	29	45
1:30	2.5		45	49	45	49	44	44	44	44	33	45
1:40	1.2		45	41	48	43	51	36	46	50	45	47

Note: T, toxic effects, i.e., cells changed morphology and/or detached from cover glass; -, not analyzed; ND, no data

* UV dose used: 20 erg/mm^2 (1 erg = 0.1 μJ); minimum of 30 nuclei scored, unless otherwise stated

** expressed as equivalent volume (mL) of original effluent per millilitre of incubation mixture